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OFFICIAL NOTICES

ELECTION OF OFFICERS AND MEMBERS OF COUNCIL

Under the revised Bye-Laws which are now operative, Officers and Members of Council— other than the President, who is nominated by Council and elected at the Annual General Meeting— are to be elected by a Postal Ballot of the members.

The attention of members is drawn to Bye-Laws Nos. 12–17 inclusive and 20–26 inclusive, which relate to Officers and Members of Council respectively.

Nominations to be valid must be received by the Honorary Secretary of the Society at least six weeks prior to the date of the Annual General Meeting, which is on 31st March 1950.

MEMBERS AND JUNIOR MEMBERS

Persons desirous of joining the Society as Ordinary Members or Junior Members may obtain Application Forms from the General Secretary or from the Honorary Secretary of any Section of the Society. Applications must be proposed and seconded by members to whom the applicants are known personally. The annual subscription is £2 2s. 0d. for Ordinary Members and 10s. 6d. for Junior Members (below 21 years of age), payable on January 1st.

The *JOURNAL*

The *Journal* is posted free to all Members and Junior Members. Non-members can obtain copies on application to the Offices of the Society. All orders must be accompanied by a remittance of 5s. 0d. per copy (£3 0s. 0d. per annum post free). Back numbers of most issues of the Society's *Journal* can be supplied at the same rate.

Members are reminded that under Bye-Law 40 the *Journal* will not be forwarded to those who have not paid their subscription by 30th June 1950.

Members residing abroad are particularly requested to inform the General Secretary by separate post when sending their subscriptions by Money Order.

Communications on any subject related to the objects of the Society, especially such as are of an original character, are invited for consideration for publication in the *Journal*. Such communications in the first instance should be addressed to the Editor, Society of Dyers and Colourists, 32–34 Piccadilly, Bradford, Yorks.

General communications, including inquiries or orders for advertisements, should be addressed to the Offices of the Society, to which address all remittances should be sent.

REPRINTS OF LECTURES AND COMMUNICATIONS

Reprints of all lectures and communications are available after publication to members and non-members of the Society. The charges (postage included) are as follows— Single copies, 1s. 6d. each; per dozen copies up to and including 8 pages, 7s. 6d., and for papers occupying more than 8 pages of the *Journal*, 10s. Orders should be addressed to "The Society of Dyers and Colourists, 32–34 Piccadilly, Bradford". They can be accepted only if accompanied by remittance and if received before the end of the month immediately following the month of issue of the paper.

ABSTRACTS SECTION

Attention is drawn to the fact that copies of the Abstracts Section of the *Journal* printed on only one side of the paper, so that individual abstracts can be cut out and pasted on cards, are available at a charge of 20s. 0d. per annum. Orders should be sent to the Society's offices at 32–34 Piccadilly, Bradford, Yorks.

FREE ADVERTISEMENTS

For the convenience of members the Publications Committee allows a limited number of advertisements relating to SITUATIONS WANTED to be inserted in the *Journal gratis*. Such advertisements must not exceed 24 words in length.

Replies may be addressed, *Box—, Society of Dyers and Colourists, 32–34 Piccadilly, Bradford, Yorks.*

NOTICE TO AUTHORS OF PAPERS

The MSS. of all papers communicated to or read before the Society become the property of the Society. They should be addressed to the Editor, Society of Dyers and Colourists, 32–34 Piccadilly, Bradford, and should be accompanied by the "Schedule of Particulars", a copy of which may be obtained from the Honorary Secretary of any Section. Authors must not allow their papers to be published elsewhere before they have appeared in the Society's *Journal*. Should prior publication take place without the sanction of the Publications Committee, the paper will be printed only as an abstract or summary.

Manuscripts submitted for publication in the *Journal* should be typewritten (double spacing) on good-quality paper, using one side of the paper only and leaving a margin at least 1 in. wide on the left-hand side. The time taken in refereeing papers (both lectures and communications) will be reduced to a minimum when authors submit two copies of the typescript. Authors are requested to be as concise as possible. When experimental procedure has already been published, a literature reference to the paper containing the details is sufficient, whilst well known experimental methods should be described very briefly.

Introductory paragraphs describing the aims of the investigation and the method of attack are desirable, and should be followed by the experimental results and their discussion. There should be a brief summary for insertion at the beginning of the paper. Centre heading should be employed sparingly. Side headings should be indented and underlined, and run into the text to which they apply by means of a dash. References to the literature should be numbered consecutively, using superscript numbers without brackets immediately following the text words or author's name to which they refer.

The list of references should be given at the end of the manuscript and the abbreviations used should be, as far as possible, those given in the "List of Periodicals Abstracted" included at the end of the Index to the preceding year's *Journal*. Reference numbers in this list should be neither enclosed in brackets, nor followed by full-stops. As far as possible throughout the manuscript the abbreviations listed on p. 54 should be used. Tables should be numbered consecutively in Roman numerals and Figures in Arabic numerals.

Figures and graphs should be carefully prepared, preferably in Indian ink, on plain white drawing paper or, preferably, Bristol board. In graphs, the frame and actual curves should be ruled and inked more heavily than any co-ordinate lines, and the latter should not be close together as in ordinary graph paper. Experimental points should always be given, and they should be indicated by small circles rather than by crosses in the case of a single graph, but where several graphs appear in a single Figure clear means of differentiation must be adopted. All numbers and legends are set up in type by the printer, and authors should therefore indicate them in pencil.

Twenty-five free copies of a reprint are supplied to the author of an original paper published in the *Journal*, or fifty free copies are supplied when there are two or more authors, and a further number may be purchased from the Society at the rates given above.

COPYRIGHT NOTICE

Original Articles, Papers, and Communications printed in this *Journal* are copyright. Subject to full acknowledgment being made, up to, but not exceeding, 800 words may be published elsewhere, but application for permission to reprint *in extenso* should be addressed to the Editor of the *Journal* at the Offices of the Society.

Lecturers are required to sign an agreement regarding the obligations in respect of copyright and publication, copies of which are supplied by the Honorary Secretaries of Sections.

The Society subscribes to the Royal Society Fair Copying Declaration (see p. 54).

LIBRARY OF THE CHEMICAL SOCIETY—LOAN OF BOOKS

Members of the Society may borrow books from the very extensive collection of works on pure and applied chemistry in the Library of the Chemical Society, by applying direct to *The Librarian, Chemical Society, Burlington House, London, W.1, and referring to their membership of the Society of Dyers and Colourists.* Letters on the subject should *not* be addressed to the Offices of the Society in Bradford.

DEPOSIT OF SEALED COMMUNICATIONS

I— The Society is prepared to receive from members and others and to keep as deposits, Sealed Communications dealing with any subject relating to the theory or practice of the Dyeing, Printing, and kindred industries.

II— Every deposit must bear on the cover a title for classification, the author's name, the date, and must be secured by a distinctive seal.

III— The deposit should be written in English, and, if it deals with machinery, be accompanied by sketches or drawings, or, in the case of dyeing or printing processes, by patterns.

IV— Every deposit will, unopened, be signed and sealed by the Honorary Secretary of the Society, immediately after receipt, and countersigned by another member of the Council.

V— The deposits will be numbered and entered into a special register, and an official receipt will be sent to the author.

VI— No charge will be made for registration and deposit.

VII— The deposits will be kept by the Society for a period of seven years. At the end of this period they will be opened and the contents read before the next meeting of the Council of the Society, and the contents, or an abstract thereof, may be published in the *Journal* of the Society at the discretion of the Publications Committee.

VIII— The author shall have the right to recall his deposit unopened at any time within the said seven years, or he may, at any time, order it to be opened and read before one of the Society's meetings. Such instructions must be accompanied by the official receipt.

IX— The Society will take every reasonable care of the deposits, but cannot be held responsible for their loss.

MEDALS AND AWARDS

HONORARY MEMBERS OF THE SOCIETY

1886–1915	*Sir H. E. Roscoe, M.P.
1886–1920	The Worshipful Master of the Dyers' Company
1886–1900	The President, Bradford Technical College
1900–1905	*W. E. B. Priestley, the Chairman of the Technical Instruction Committee of the Bradford City Council
1902–1926	*F. H. Bowman, D.Sc., F.I.C., F.R.S.E.
1908–1916	*Prof. Dr. C. Graebe
1908–1915	*Prof. Dr. C. Liebermann
1911–1916	*Prof. Adolf von Baeyer
1914–1924	*Count Hilaire de Chardonnet
1917–1941	*Arthur G. Green, M.Sc., F.I.C., F.R.S.
1919–1938	*R. Vidal
1920–	The Prime Warden of the Worshipful Company of Dyers
1921–1930	*Horace A. Lowe
1923–1935	*Charles F. Cross, F.R.S.
1925–1927	*Maurice Prud'homme
1927–1930	*Ernest Hickson
1928–1939	*R. E. Schmidt
1931–1933	*Alfred Rée, Ph.D.
1932–1940	*W. M. Gardner
1934–1947	*George Douglas
1934–1946	*H. Grandage
1934–1940	*Christopher Rawson
1941–1948	*Prof. E. C. C. Baly, C.B.E., M.Sc., F.R.S.
1944–1946	*Prof. F. M. Rowe, D.Sc., F.R.I.C., F.R.S.
1946–1946	*James S. Ridsdale
1947	C. J. T. Cronshaw, D.Sc., F.R.I.C., M.I. Chem.E., F.T.I., F.R.S.E.
1948	H. Jennison, M.C., A.M.C.T., A.R.I.C.

THE PERKIN MEDAL

The Perkin Medal was modelled by the late F. W. Pomeroy, R.A., for the Society. It is an excellent presentation of the head of Sir William Perkin, the founder of the coal-tar colour industry, and President of the Society in 1907.

This medal is awarded at intervals of two or three years for discoveries or work of outstanding importance in connexion with the tinctorial arts.

LIST OF RECIPIENTS

1908	Professors Graebe and Liebermann. "Synthesis of Alizarin."
1911	Prof. Adolf von Baeyer. "Synthesis of Indigo."
1914	Comte Hilaire de Chardonnet. "Artificial Silk."
1917	Prof. Arthur G. Green. "Primuline."
1919	R. Vidal. "Sulphur Black."
1921	Horace Lowe. "Permanent Lustre on Cotton."
1923	Chas. F. Cross. "Discovery of Viscose."
1925	M. Prud'homme. "Aniline Black and Alizarin Blue."
1928	Dr. Robert E. Schmidt. "For Epoch-making Discoveries of Anthraquinone Derivatives and Dyestuffs therefrom."
1938	Dr. H. Dreyfus. "For Discoveries and Work of Outstanding Importance in Connection with the Development of the Cellulose Acetate Rayon Industry in England."
1938	J. Baddiley. "In Recognition of his National Services for the Renaissance of the British Dyestuffs Industry through Many Important Investigations in the Field of Colour Chemistry Conducted or Directed by him."

THE MEDAL OF THE SOCIETY OF DYERS AND COLOURISTS

This Medal was instituted by the Society in 1908. Of the competitive designs submitted, that of Mr. Edgar Lockwood was selected. The design indicates that the work of the dyer (centre figure) is both a science (right background) and an art (left foreground).

1908–1927	The Medal was occasionally awarded as a recognition of work of exceptional merit carried out under the Society's Research Scheme.
From 1928	The Medal was awarded as a recognition of exceptional services (*a*) to the Society or (*b*) in the interests of the Tinctorial and Allied Industries.

LIST OF RECIPIENTS

1908	J. B. Fothergill (Bronze Medal). "Treatment of Cotton to Cause it to Resist Direct Dyeing Colours."
1912	J. H. Garner (Silver Medal). "Treatment of Effluents from Dyehouses and Textile Factories."
1928	Ernest Hickson (Gold Medal). "Exceptional Services rendered to the Society as Chairman of the Publications Committee 1897–1925, and Chairman of *Colour Index* Committee."
1930	Arthur Silverwood (Gold Medal). "Exceptional Services rendered to the Society as Honorary Secretary 1913–1930."
1933	Prof. Walter M. Gardner (Gold Medal). "Distinguished Services as Editor of the Society's *Journal* 1900 to 1932."
1934	Prof. F. M. Rowe (Gold Medal). "Exceptional Services to the Society and to the Tinctorial Industries as Editor of the *Colour Index* 1924 and the 'Supplement' 1928."
1934	L. A. Lantz (*Chairman*), H. H. Bowen, P. W. Cunliffe, R. S. Horsfall, Prof. B. A. McSwiney, C. C. N. Vass, C. M. Whittaker, S. G. Barker (Silver Medals). "Exceptional Services to the Society as Members of the Standardisation of Fastness Executive Committee."
1936	W. A. Edwards (Silver Medal). "Valuable Services rendered to the Society as Honorary Secretary of the Midlands Section since its inception in 1919 to 1935."
1937	R. Ritchie (Silver Medal). "Devoted and Valuable Services as Honorary Secretary of the Scottish Section for eighteen years."
1940	F. L. Goodall (Gold Medal). "Valuable Services to the Tinctorial Industries by his work on the Theory and Practice of Wool Dyeing."

HOME ECONOMICS

1943 C. M. Whittaker (Gold Medal). "In recognition of Exceptional Services in promoting Scientific and Technical Knowledge amongst Textile Colourists, and for Sustained and Outstanding Service to the Society."

1946 H. H. Bowen (Gold Medal). "For Outstanding Services to the Society and in recognition of his Chairmanship of the Publications Committee for a period of twenty years."

H. H. Hodgson (Gold Medal). "For Outstanding Services to the Society and for his series of Sustained Experimental and Theoretical Contributions to those chapters of Organic Chemistry which are the essential scientific background to the Dyestuffs Industry."

E. Race (Silver Medal). "For his Valued Services to the Society as Joint Author of thirteen papers published in the Society's *Journal*."

H. Turner (Silver Medal). "In recognition of his Valuable Services to the Society and of his twenty-two years' service as Honorary Secretary of the Huddersfield Section."

Mrs. E. Cummings (*née* Levin) (Silver Medal). "For her Valued Services to the Society; by her assistance rendered in the preparation of the first *Colour Index*; by her Joint Authorship of a number of Papers published in the *Journal* of the Society, and as an Abstractor for the *Journal* of the Society for twenty years."

1947 Fred Smith (Gold Medal). "For Exceptional Services to the Society over a period of thirty-seven years comprising Chairman, West Riding Section; Member of Council and of many important Committees."

F. Scholefield (Gold Medal). "In recognition of Exceptional Services to the Society in the advancement of Tinctorial Technology both in theory and practice."

C. Schardt (Silver Medal). "In recognition of his Valuable Services to the Society over a period of twenty-four years including Chairman, Vice-Chairman, and member, of the Midlands Section Committee."

1948 G. G. Hopkinson (Gold Medal). "For Valuable Services rendered to the Society and to the Dyeing Industry."

D. B. F. McAndrew (Silver Medal). "For Valuable Services rendered to the Society as Honorary Secretary and Committee Member of the Scottish Section 1935–1947."

C. O. Clark (Silver Medal). "For Valuable Services rendered to the Society from 1923 to 1948."

1949 S. M. Neale (Gold Medal). "For his Pioneer Work in the Application of the Methods of Physical Chemistry to the Elucidation of the Phenomena of Dyeing, more particularly of Cellulosic Materials with Substantive Dyes."

THE WORSHIPFUL COMPANY OF DYERS RESEARCH MEDAL

The Medal represents the Arms of the Worshipful Company of Dyers of the City of London, which were granted in 1471. The following is a brief description—

Arms— Sable, a chevron engrailed argent, between three bags of madder of the last, corded or.

Crest— On a wreath three sprigs of the graintree erect vert, fructed gules.

Supporters— Two leopards rampant gardant argent, spotted with various colours; fire issuing from their ears and mouth proper, both ducally crowned or.

Motto— Da Gloriam Deo.

1— The Dyers' Company offer annually a Gold Medal called "The Worshipful Company of Dyers Research Medal", the award of which is open to the Authors of papers embodying the results of scientific research or technical investigation connected with the tinctorial arts submitted to the Society of Dyers and Colourists, and published in the *Journal* of such Society during the twelve months ending on the 30th June in the year for which the Medal is granted, and, in the special circumstance provided for by Rule 6, during the twelve months ending on the 30th June in the year previous to that for which the Medal is granted. If a paper shall be published in two or more parts, then for the purpose of the award of the Medal, all the parts together shall be treated as a paper published in the year in which the final part is published.

2— The Medal will not be awarded to the same person on more than one occasion.

3— The Society of Dyers and Colourists shall consider the papers available for the Medal and advise the Company as to the merits thereof, and if, in the judgment of the Society, none of the papers is of sufficient merit, the Society may recommend that the Medal be not awarded.

4— The Dyers' Company will award the Medal either to the Author of the paper which, in all the circumstances, appears to the Company to show the greatest merit, or, in the event of such paper being the work of an Author who has already been awarded the Medal, to the Author of the paper next in order of merit who has not already been awarded the Medal, and may, if the Company so thinks fit, refrain from making any award.

5— In the event of a paper being the work of two or more persons, the Author shall be taken to be that one of them whose work in the opinion of the Society of Dyers and Colourists has most substantially contributed to the merit of the scientific research or technical investigation embodied in such paper.

6— In the event of the Author of a paper of sufficient merit published in the *Journal* of the Society of Dyers and Colourists during any twelve months for which the Medal is awarded being unsuccessful in obtaining the award of the Medal for that period, the Society of Dyers and Colourists may, in their discretion, consider such paper for adjudication with the papers available for the award of the Medal for the next succeeding twelve months.

LIST OF RECIPIENTS

1908 Prof. E. Knecht. "A Means of Estimating the Degree of Mercerisation in Cotton Yarns."

1909 Prof. Arthur G. Green. "The Chemical Technology of Aniline Black."

1910–11 R. L. Taylor. "The Action of Carbon Dioxide and of Air on Bleaching Powder."

1911–12 W. Harrison. "The Electrical Theory of Dyeing."

1912–13 S. H. Higgins. "Observations on the Bleaching of Cotton" and "The Action of Neutral Salts on Bleaching Solutions."

1913–14 W. Johnson (in conjunction with Prof. Arthur G. Green, who had already been awarded the Medal). "The Constitution of Aged and of Bichromate Aniline Blacks."

1914–15 Morris Fort. "The Mechanism of the Acid Dyebath."

1915–16 James R. Hannay. "The Interaction between Metallic Copper and certain Dyes of the Thiazine, Oxazine and Azine Series."

1916–17 Prof. H. M. Dawson. "The Phenomena of Acid Catalysis and the Theory of Acids."

1917–18 L. G. Radcliffe. "The Sulphonation of Fixed Oils."

1918–19 Chas. F. Cross (Diplomas presented to M. C. Lamb and C. V. Greenwood as co-authors). "Colloidal Tannin Compounds and their Applications."

1919–20 A. E. Everest (Diploma presented to A. J. Hall as co-author). "The Tinctorial Properties of some Anthocyans and certain Related Compounds."

1920–21 Prof. G. T. Morgan. "The Co-ordination Theory of Valency in Relation to Adjective Dyeing."

1921–22 S. Judd Lewis. "On the Fluorescence of Cellulose and its Derivatives."

1922–23 Prof. Arthur G. Green (Bar attached to Medal previously awarded), and K. H. Saunders. "The Ionamines— A New Class of Dyestuffs for Cellulose Acetate Silk."

1923–24 S. Judd Lewis (Bar attached to Medal previously awarded). "The Quantitative Determination of the Fluorescent Power of Cellulose and its Derivatives."

1924–25 Prof. F. M. Rowe (with Diploma to Miss C. Levin, as co-author). "The Identification of Azo Colours on the Fibre and of Azo Pigments in Substance."

1925–26 H. H. Hodgson. "Behaviour of the Sulphides of Sodium in Aqueous and Alcoholic Media", and "The Action of Sulphur on the Monochloranilines."

1926–27 Prof. F. M. Rowe (Bar attached to Medal previously awarded) and Diplomas awarded to collaborators— Miss E. Levin, A. C. Burns, J. S. H. Davies, and W. Tepper. "A New Reaction of Certain Diazosulphonates derived from β-Naphthol-1-sulphonic acid, leading to the preparation of Phthalazine, Phthalazone and Phthalimidine Derivatives."

1927–28 No award.

1928–29 F. Scholefield (with Diplomas to Miss E. Hibbert and C. K. Patel as co-authors). "The Action of Light on Dyed Colours."

1929–30 H. H. Hodgson (Bar attached to Medal previously awarded). "Colour and Constitution from the Standpoint of Recent Electronic Theory."

1930–31 Prof. F. M. Rowe (Second Bar attached to Medal previously awarded), and Diplomas awarded to S. Ueno and F. H. Jowett as collaborators. "Insoluble Azo Colours on the Fibre and Action of Boiling Caustic Soda thereon."

1931–32 No award.

1932–33 Two awards— W. T. Astbury. "The X-ray Interpretation of Fibre Structure."
J. B. Speakman. "The Structure of the Wool Fibre; its Relation to the Dyeing and Finishing Processes of the Wool Textile Trade."

1933–34 No award.

1934–35 H. A. Turner, and Diplomas awarded to G. M. Nabar and F. Scholefield, as co-authors. "The effect of Reduced Vat Dyes upon the Hypochlorite Oxidation of Cellulose."

1935–36 Prof. F. M. Rowe (Third Bar attached to Medal previously awarded), and Diplomas awarded to C. H. Giles, R. L. M. Allen, W. G. Dangerfield, and Glyn Owen, as collaborators. "Decomposition of Azo Dyes by Acids, Caustic Alkalis, and Reducing Agents."

1936–37 J. B. Speakman (Bar attached to Medal previously awarded), and Diplomas awarded to C. S. Whewell and J. L. Stoves, as collaborators. "The Reactivity of the Sulphur Linkage in Animal Fibres."

1937–38 Prof. F. M. Rowe (Fourth Bar attached to Medal previously awarded), and J. B. Speakman (Second Bar attached to Medal previously awarded), and Diplomas awarded to E. Race and T. Vickerstaff, as collaborators. "The Unlevel Dyeing of Wool with Acid and Chrome Dyes. Part I— The Reasons for the Uneven Dyeing Properties of Wool Staples and of Cloth Damaged by Exposure, and Part II— A Method for Correcting the Uneven Dyeing Properties of Wool Staples and of Cloth Damaged by Exposure."

1938–39 No award.

1939–40 T. H. Morton, as senior author of the paper on "Application of Vat Dyes to Viscose Rayon", by J. Boulton and T. H. Morton.

1940–41 No award.

1941–42 T. Vickerstaff, as senior author of the paper on "The Dyeing of Cellulose Acetate Rayon with Dispersed Dyes", by T. Vickerstaff and E. Waters.

1942–43 No award.

1943–44 J. Boulton. "The Importance of Dyeing Rate— an Interpretation for the Practical Dyer of Recent Research on Direct Dyeing."

1944–45 No award.

1945–46 No award.

1946–47 H. Phillips, as senior author of the paper on "The Chemical Constitution and Physical Properties of Bisulphited Wool", by E. G. H. Carter, W. R. Middlebrook, and H. Phillips.

1947–48 J. M. Preston, "Some Factors Affecting the Dyeing of Viscose" and "Some Aspects of the Drying and Heating of Textiles".

1948–49 H. Lindley, as major contributor to the paper "The Mechanism of Set and Supercontraction in Wool Fibres", by S. Blackburn and H. Lindley.

THE WORSHIPFUL COMPANY OF FELTMAKERS RESEARCH MEDAL

The Feltmakers' Company offer annually a Gold Medal for Papers embodying the results of scientific research or technical investigation connected with the art of feltmaking and published in the *Journal* of the Society. Further, in order to encourage research of a type likely to qualify for the award of the Medal, the Feltmakers' Company offer annually, for an initial period of five years, a Research Grant of £50.

January 1945–June 1946 No award.
July 1946–June 1947 No award.
July 1947–June 1948 No award.
July 1948–June 1949 No award.

KNECHT MEMORIAL FUND

A Fund of £100 was subscribed as a Memorial to the late Professor Edmund Knecht from the interest on which two prizes, in the form of books, are awarded annually to selected students of the Manchester College of Technology and the Royal Technical College, Salford.

MERCER LECTURES

A sum of £20 per annum is being given to the Society for a limited period of years in commemoration of the centenary of the discovery of mercerisation. Suitable lecturers are invited to give a Mercer Lecture annually.

LECTURERS

1944 N. G. McCulloch and G. S. Hibbert. "Science in an Old Industry."

1945 G. S. J. White, B.A., and T. Vickerstaff, Ph.D. "Colour."

1946 D. Entwistle, B.Sc., A.R.I.C. "Regenerated Fibres from Natural Polymers."

1947 E. J. Bowen, M.A., F.R.S. "Colour and Constitution— The Absorption of Light by Chemical Compounds."

1948 F. Farrington, B.Sc., F.R.I.C. "Textile Printing."

1949 E. Wilson, B.A. "Some Applications of Chemistry to Textile Finishing."

GEORGE DOUGLAS LECTURE

1949 H. Levinstein, M.Sc., Ph.D., M.I.Chem.E., F.R.I.C. "George Douglas, His Times, and Some Thoughts on the Future."

Proceedings of the Society

MANCHESTER AND SCOTTISH SECTIONS

Meetings held at the Gas Department Showrooms, Manchester, on 21st November 1947, Dr. J. C. WITHERS in the chair (joint meeting with the Lancashire Section of the Textile Institute); and at the Royal Technical College, Glasgow, on 27th January 1948, Mr. J. A. YOUNG in the chair

The Effect of Physical Pretreatment on the Ease of Saponification of Cellulose Acetate Material

C. P. TATTERSFIELD

Introduction

During work on the saponification of Seraceta (Courtaulds) fabrics, early in 1943, it was observed that parts of the fabric to which pressure had been applied saponified more readily than the remainder of the fabric when caustic soda was used as the saponifying agent. Further work showed this to be a general phenomenon, the effect of straining a yarn or fabric, by either tension, pressure, or abrasion, being to increase the ease with which saponification took place in those parts. It was also observed that prior treatment of commercial acetate yarns and fabrics by hot water, or preferably by hot common salt solution, reduced the ease of saponification of the whole fabric and also eliminated any particular tendency to saponification induced by strain. Caustic potash was found to behave similarly to caustic soda, but saponification by hot sodium carbonate or ammonia solution failed to show where strains had been introduced.

Whilst most of the work was carried out on Seraceta yarn or fabric, similar effects were produced on other cellulose acetate yarns and fabrics and also on cellulose acetate film.

In this paper the effects of variations in procedure are described and also the possible uses of these observations, firstly in producing effects by differential saponification followed by dyeing, secondly in the detection and identification of faults in yarns or fabrics, and thirdly in helping to elucidate the surface structure of commercial cellulose acetate materials.

Experimental

Most of the work has been carried out on 140/28 or 150/30 Seraceta yarn. Work on fabric has been conducted on Seraceta satin.

Unless otherwise stated, treatments have been carried out in 40 volumes of liquor.

The degree of saponification has been measured by the increase in affinity of the material for direct cotton dyes. All materials were dyed for 30 min. at 80°C. with—

1% ... Diphenyl Brilliant Blue FF 200 (*C.I.* 518)
10% ... Common salt

washed off in cold water, and then dried. Prior to dyeing, all saponified materials were washed off thoroughly in cold and then hot water. They were then steeped in dilute acetic acid and again thoroughly rinsed with cold and hot water.

The caustic soda used was of commercial quality of 70° Tw. containing 45 g. NaOH per 100 c.c. The soda ash was I.C.I. commercial quality of 98–99% Na_2CO_3 content.

EFFECT OF CONDITIONS OF SAPONIFICATION

Seraceta satin fabric was used in order to determine the effect of variations in conditions of saponification on the degree of saponification of ground and also of impressed effects. These impressed effects were produced by drawing lines across the fabric with a pencil or glass rod. The pressure was applied as evenly as possible, and the fabric was then cut into sufficient pieces to carry out one set of tests.

CONCENTRATION OF CAUSTIC SODA— The pieces of marked fabric were steeped for 5 min. in various concentrations of caustic soda, and then subjected to the standardised neutralising and washing procedure. The results obtained after dyeing are given in Table I.

TABLE I
(see Fig. 1)

	Concentration of Caustic Soda (c.c. of 70° Tw. NaOH per 100 c.c.)	Degree of Saponification	
		Ground	Effect
(*a*)	2	None	Very slight
(*b*)	5	Slight	Medium
(*c*)	10	Very heavy	Effect obscured
(*d*)	20	Cloth practically destroyed	
(*e*)	50	Medium	Medium–heavy
(*f*)	100	Slight	Slight–medium

The differential effect is obtained even with the highest concentrations of caustic soda (Fig. 1). The decrease in saponification with increase in concentration of caustic soda above an optimum value is well known in connection with the mercerising of cotton in the presence of cellulose acetate rayon.

TIME— Pieces of marked fabric were steeped for various lengths of time in various strengths of caustic soda, neutralised, washed off, and dyed, with the results given in Table II.

TABLE II

Concentration of Caustic Soda (c.c. of 70° Tw. NaOH per 100 c.c.)	Time (min.)	Degree of Saponification	
		Ground	Effect
1	10	None	Very slight
1	30	Very slight	Medium
2	2	None	None
2	10	Very slight	Medium
2	30	Heavy	Effect obscured

TEMPERATURE— Marked pieces of Seraceta fabric were treated as indicated in Table III, and then dyed by the usual procedure.

TABLE III

Concentration of Caustic Soda (c.c. of 70° Tw. NaOH per 100 c.c.)	Time (min.)	Temperature (°C.)	Degree of Saponification	
			Ground	Effect
0·2	30	60	Very slight	Slight–medium
2	10	20	Very slight	Medium
2	10	60	Heavy	Obscured

It will be noted that the most dilute solution of caustic soda at 60°c. gives a similar effect in 30 min. to that obtained with a tenfold increase in caustic soda concentration at 20°c. for 10 min.

ADDITIONS TO CAUSTIC SODA— With the 0·2% caustic soda (0·2 c.c. of 70° Tw. NaOH per 100 c.c.) at 60°c., addition of common salt or sodium acetate increases the degree of saponification of both ground and effect.

USE OF OTHER ALKALIS TO PRODUCE DIFFERENTIAL SAPONIFICATION— (1) *Potassium Hydroxide*— Seraceta yarns and fabrics were saponified for 10 min. with concentrations of 1–40% potassium hydroxide in the cold. Dyeing with direct dyes indicated that the degree of saponification was a maximum with between 5% and 10% solution and, as with caustic soda, both above and below these concentrations strained material saponified somewhat more than unstrained.

(2) *Ammonia*— Steeping in ammonia (sp.gr. 0·88) for 10 min. in the cold failed to produce any apparent saponification of either strained or unstrained cellulose acetate.

(3) *Soda Ash*— Marked pieces of fabric were steeped in soda ash solution at concentrations of 0·6–30% and temperatures of 20–90°c. and then dyed with direct cotton dyes.

In no instance was any differential effect produced; i.e. pressure-marked areas did not saponify more readily than the unmarked parts.

It was noted that strong solutions of soda ash at high temperatures failed to produce saponification of the fabrics. Similarly, a weak solution (3%) in a strong solution of common salt (30%) also failed to produce saponification, although the same concentration in the absence of salt did so. It therefore appears that a "salt effect" may be operative with strong solutions of soda ash. The effect of salt treatment on the ease of saponification of cellulose acetate materials is discussed later.

EFFECT OF METHOD OF PRODUCING STRAIN

In the experimental matter described up to now, strain has been produced in cellulose acetate materials by the application of pressure. Strain produced in any other way, however, also induces an increased tendency to saponify.

PRESSURE— Cellulose acetate fabrics and film have been subjected locally to pressure by running smooth and rough objects over the surface, such objects including pencil points, rounded glass rods, and metal discs either secured or freely rotating. Fabric and film have been pressed between engraved rollers and have also been subjected to more sudden impacts such as striking with a hammer or with typewriter keys. In all cases the strained part has saponified more readily than the remainder of the material, when steeped in cold dilute caustic soda. The extent of this increased ease of saponification depends on the pressure applied and on other factors.

ABRASION— Cellulose acetate fabric abraded by gentle rubbing of the surface with an indiarubber or with sandpaper saponifies more readily than the unabraded part. A very striking effect is produced by saponifying together normal and commercial abraded yarn, and then dyeing with direct cotton or mixed direct cotton and dispersed acetate dyes. The saponification can be controlled to give the abraded yarn a high affinity for the direct dye whilst the normal yarn has virtually none (Fig. 2). Similarly, cellulose acetate film can be locally sandpapered, partly saponified, and then dyed with cotton dyes to give striking effects (Fig. 3).

STRETCHING — Experiments with cellulose acetate yarns have shown that, if commercial yarns are stretched, they are more readily saponified. As stretch is more easily measurable than pressure or abrasion, the effect of variations in its production has been studied in greater detail.

For these experiments 5-g. hanks of 42 in. reel of 150/30 Seraceta were used. They were stretched between two rods at an even slow rate, and after the required degree of stretch had been obtained the yarns were held for 1 min. before releasing the tension.

The ease of saponification was measured as before, by steeping in caustic soda solution (2 c.c. of 70° Tw. per 100 c.c.) for a specified time, and then thoroughly washing, neutralising, and dyeing with Diphenyl Brilliant Blue FF 200.

Effect of Degree of Stretch— Hanks were stretched 5%, 10%, 15%, 20%, and until broken. It appeared from the dyeing tests that ease of saponification increased up to 15% stretch, but was constant above this figure.

The figures of acetyl content of these yarns given in Table IV, however, indicate that the degree of saponification increases with degree of prestretch up to 20%. The overall increase is, however, less than the increase in absorption of direct dye might have led one to expect.

TABLE IV

Degree of Stretch prior to Saponification (%)	Acetyl Value
0	49·08
5	49·89
10	47·84
15	47·18
20	46·45
Until broken	46·64

EFFECT OF AQUEOUS TREATMENTS ON THE EASE OF SAPONIFICATION OF NORMAL AND STRAINED CELLULOSE ACETATE MATERIALS

Whilst it has been generally appreciated that hot-water treatment modifies cellulose acetate yarn to some extent, in this present work it was observed that, not only did such treatment greatly decrease the ease of saponification of unstrained cellulose acetate yarns, fabrics, and films, but it also removed any predisposition of strained materials to saponify more readily than unstrained.

The effect of aqueous treatment was first observed when unscoured fabric made from a sized warp and an unsized weft was saponified. The warp did not saponify as readily as the weft, and it was concluded that the size was exerting a protective action (Fig. 4). The effect of scouring was

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not, however, to make the warp saponify as quickly as the weft, but rather to reduce the rate of weft saponification to that of the warp. Sizing had apparently reduced the rate of saponification of the warp, and the hot scouring liquors subsequently reduced the rate of saponification of the weft to a similar degree.

To discover the optimum conditions for improving the resistance to saponification of cellulose acetate, hanks of 150/30 Seraceta were treated in various aqueous media, and the ease of saponification was found by steeping in caustic soda solution (2 c.c. of 70° Tw. per 100 c.c.) at 20°c. for various lengths of time, and then washing off, neutralising, and finally dyeing with Diphenyl Brilliant Blue FF.

Addition of Salt to the Pretreatment Liquor— Hanks were treated in water, in 5, 10, 15, 20, 25, and 30% solutions of common salt, and in a 30% solution of sodium acetate at 90°c. for 10 min. It was found that water had the least effect on the ease of saponification and that the optimum effect was obtained with concentrations of 15–25% of common salt. Sodium acetate behaved similarly to common salt.

Acetyl values of yarns, saponified with cold caustic soda solution (2 c.c. of 70° Tw. per 100 c.c.) for 45 min., illustrate this effect very clearly (Table V). In terms of decrease in acetyl content the figures become even more striking.

Table V

Pretreatment	Acetyl Value	Decrease
Original value	53·9	—
None	26·83	27·07
Water at 90°c. for 10 min.	47·90	6·0
30% salt solution at 90°c. for 10 min.	51·94	1·96

Temperature of Pretreatment— Hanks were treated at temperatures of 20–90°c. in a 30% salt solution for 10 min. Treatments below 60°c. had little effect on the ease of saponification, but above 60°c. increase in temperature progressively reduced the ease of saponification. Yarn treated at 90°c. in 30% salt solution saponified less after 40 min. than untreated yarn saponified for 10 min.

Effect of Salt Treatment on the Saponification of Strained Cellulose Acetate Materials— If cellulose acetate materials, yarns, fabrics, or films strained in any of the ways previously described, by pressure, by abrasion, or by stretching, are treated in hot concentrated salt solution, any tendency for the strained parts to saponify more readily than the remainder of the material is removed. For example, a cellulose acetate film, the surface of which has been scratched, will show signs of saponification after a 10-min. treatment at 20°c. in caustic soda (2 c.c. of 70° Tw. per 100 c.c.), and the scratched part will then be heavily saponified. If the film is treated in 30% salt solution for 30 min. it may then be treated with caustic soda under the above conditions for 40 min. before showing a similar degree of saponification, and the scratch is not more heavily saponified than the ground (Fig. 5).

It will be noted that, whilst after the hot salt treatment the obvious physical effect of the strain remains, e.g. increased length of stretched yarns, rough surface of abraded yarns, or scratches on film, the increased ease of saponification originally associated with these effects is no longer present (Fig. 6).

If unstrained materials which have received a hot water or hot salt treatment are subsequently strained in any of the previously described ways, then on saponification the strained parts will saponify more readily than the unstrained. For example, hanks of 150/30 Seraceta, stretched from 0% to breaking (over 20%), showed slight–heavy saponification after 15 min. treatment in dilute caustic soda. Similar hanks were treated in hot salt solution, washed, dried, and conditioned prior to stretching. On saponifying as before, the unstretched showed no saponification, but with increasing stretch increasing saponification was observed, the degree being in general similar to that obtained on the unpretreated yarn. Acetyl values again illustrate this point (Table VI).

Table VI

Effect of Salt Treatment on Acetyl Values after Caustic Soda Treatment
(Original value 53·9)

Stretch (%)	Not Salt-treated	Salt-treated	
		Before Stretching	After Stretching
0	49·08	51·25	51·25
5	49·89	—	51·12
15	47·13	49·08	—
Until broken	46·65	45·86	50·48

Appreciation of this marked retardation of saponification by hot aqueous pretreatment may have some value in the dyeing of vat dyes on mixtures of viscose rayon and acetate rayon, when it is desired to reserve the acetate rayon. The best reserves will be obtained when the fabric or yarn has received a thorough hot wet treatment (either as part of the scour or as a separate process) prior to dyeing.

Potential Uses of Techniques

Examination of Variation in Materials

Very often yarns, fabrics, and films may be subjected to physical strain; unless such effect is marked, examination by known methods is not easy. Provided the material has not received any hot wet treatment or steaming subsequent to straining, the present technique offers a very delicate test for any variation due to the physical treatment of the material.

For example, uneven stretch in a yarn can be identified. A yarn or cord which has been tightly knotted and then unknotted will show definite strain marks. There is no difficulty in deciding whether a yarn or fabric has been ruptured or cut, since in the former case strain marks will be visible to an appreciable distance into the material, whereas in the latter the strain is localised to the very edge (Fig. 7 and 8). Similarly, a cellulose acetate film folded and broken at the fold will show a different effect from one cut with a knife or scissors (Fig. 9). Even severe folding of an acetate film with subsequent straightening can be shown up by the partial saponification technique (Fig. 10).

By an extension of the test it is possible to decide whether a fault is due to physical strain of the types

considered or to some other cause. If partial saponification and dyeing indicate the presence of a fault or faults, a further piece of the original material should be treated in hot salt solution, and then partly saponified and dyed. If the fault is no longer apparent, then it may reasonably be assumed to be due to physical strain. If it still exists, then it must be due to another cause. Two examples may be cited—

Firstly a white cellulose acetate dance dress was examined. After dry-cleaning, a number of small holes were apparent round the bottom of the skirt. It was suggested that these might be due to termites, although no holes were noticed before cleaning and termites do not often attack cellulose acetate fabrics. We were not able to cut the dress up, but small pieces of fabric surrounding one or two holes were examined by the partial saponification technique, and bruise marks, not before apparent, were found leading up to and all round the holes. It therefore appeared that damage had been caused by bruising, probably from numerous buttons present on the dress, and probably during the cleaning process (Fig. 11).

The second example concerns a Seraceta twist yarn which, when vat-dyed by the caustic–bicarbonate method, was locally dulled and uneven. The distribution of dulling was not readily apparent, but partial saponification of an undyed hank showed four patches evenly distributed round the hank, coinciding with arms of the swift on which the hanks had been steamed. This fault, however, persisted after a salt "annealing" treatment, so that it was due to causes other than purely physical strain.

In the course of this particular investigation, the virtual impossibility of even steaming of acetate yarns in bobbin form was observed. A bobbin steamed for 90 min. was hanked, partly saponified, and dyed with direct dyes. The outside of the bobbin was undyed, indicating the annealing effect of the steam, whereas the inside was dyed as heavily as an unstrained hank.

DEVELOPMENT OF EFFECTS

From the foregoing it will be obvious that it should be possible to submit cellulose acetate materials to local strain and then saponify them to such an extent that the strained part will be sufficiently saponified to be dyed with cotton dyes, whilst the unstrained part is not. On acetate fabrics, effects of this nature have been produced chiefly in two ways— firstly by passing through embossing rollers, or through plain rollers along with a fabric of marked design, this design being thereby impressed on to the acetate fabric (Fig. 12 and 13); and secondly by submitting the fabric to sharp local blows, a typewriter key being suitable on the small scale (Fig. 14 and 15).

Fabric must be prepared and scoured before embossing, since this will not only cleanse the fabric, but also remove any undesirable strains which may be present. After embossing, the fabrics must not undergo any hot wet treatment or steaming, and, of course, must not be subjected to any uneven strain.

The possibility of obtaining effects by the use of abraded yarns and normal yarns has been discussed. The use is limited, since any abraded yarn must not be sized or steamed, etc., and fabrics containing it must not be scoured prior to saponifying unless such processes can be carried out at low temperatures.

With knitted fabrics, which normally are not sized and which may be in a suitable state for dyeing without preliminary scouring, there is more possibility of producing effects of this type using normal and abraded yarns.

Whilst any direct dye or solubilised vat dye of the Soledon type may be used to produce the dyed effect, some appear to be more suitable than others, and the results of trials with a number of them are given in Tables VII and VIII. The fastness obtained is that of the dye applied to cellulose.

TABLE VII
Direct Cotton Dyes

Dye	*Colour Index* No. or Maker	Staining of Ground	Clarity of Effect
Diphenyl Chlorine Yellow FF	814	Medium	Medium–poor
Chlorazol Fast Orange AGS...	ICI	Medium	Medium
Direct Fast Orange SE ...	326	Medium	Good
Direct Fast Scarlet SE ...	326	Medium	Good
Diphenyl Fast Red 7BL 180	Gy	Medium	Good
Chlorazol Fast Helio BK ...	319	Medium–heavy	Good
Diphenyl Brilliant Blue FF...	518	Very slight	Good
Rigan Sky Blue G	Ciba	None	Good
Diphenyl Blue M2B ...	Gy	Very slight	Medium–good
Chlorantine Fast Blue GLL...	Ciba	None	Medium
Durazol Blue 8GS	ICI	None	Poor
Chlorazol Fast Black BK ...	ICI	Medium–heavy	Good
Chlorantine Fast Green 5GLL	Ciba	Medium	Medium–good
Solophenyl Red Brown ...	Gy	Medium	Medium–poor
Benzanil Fast Brown 5RL...	YDC	Medium–heavy	Good
Chlorazol Brown PBS ...	ICI	Medium	Good

TABLE VIII
Solubilised Vat Dyes

Dye	*Colour Index* No. or Makers	Salt (%)	Staining of Ground	Clarity of Effect
Soledon Yellow 5GS ...	ICI	200	Heavy	Poor
Soledon Yellow GS paste ...	ICI	120	Very heavy	Fair
Soledon Gold Yellow RKS	ICI	80	Medium	Poor
Soledon Orange 4RS ...	ICI	120	Medium	Good
Soledon Pink FFS	ICI	200	Heavy	Good
Indigosol Red IFBB ...	DH	120	Slight	Good
Indigosol Violet ABBF ...	DH	160	Very heavy	Good
Soledon Dark Blue 2RS ...	ICI	40	Medium	Good
Soledon Blue 4GS	ICI	160	Heavy	Good
Indigosol 04B	1184	120	Heavy	Good
Soledon Blue 2RCS... ...	ICI	200	Very slight	Poor
Soledon Green GS	ICI	80	Slight	Good
Soledon Green 5GS ...	ICI	80	Heavy	Good
Soledon Jade Green XS ...	ICI	10	Medium	Good
Indigosol Brown IRRD ...	DH	40	Slight	Good
Soledon Dark Brown 2RS...	ICI	120	Slight	Good

Further tests indicated that better effects could be obtained by dyeing at the temperature at which the dye has maximum affinity for viscose rayon; e.g. with Soledon Pink FFS cold dyeing gave the best contrast.

Effects of a similar nature can be produced on cellulose acetate sheet, although here the implication of sizing, steaming, and scouring need not be considered.

The difficulty in applying the technique is that each sample must be treated individually. It is

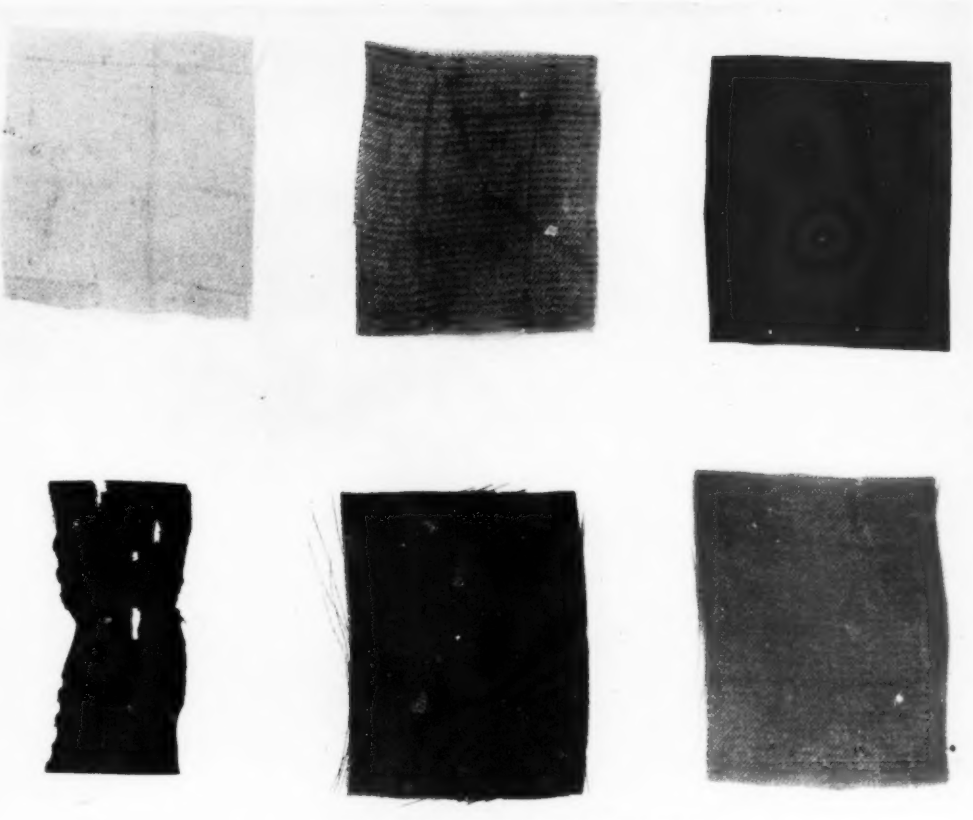


FIG. 1— Cellulose Acetate Fabric pressure-marked, treated with Varying Concentrations of Caustic Soda, and then dyed with Diphenyl Brilliant Blue FF and Dispersol Fast Yellow A

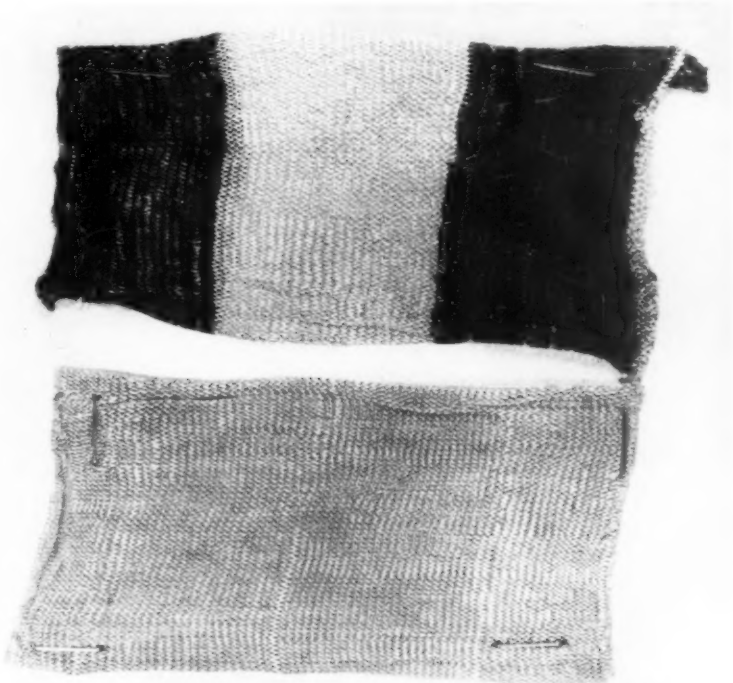


FIG. 2 (TOP)— Knitted Panels of Abraded Acetate Yarn (outer panels) and Normal Acetate Yarn (centre), partly saponified and then dyed with direct dyes and dispersed acetate dyes

(BOTTOM)— Similar Panels treated in Boiling 20% Salt Solution prior to Saponification and Dyeing

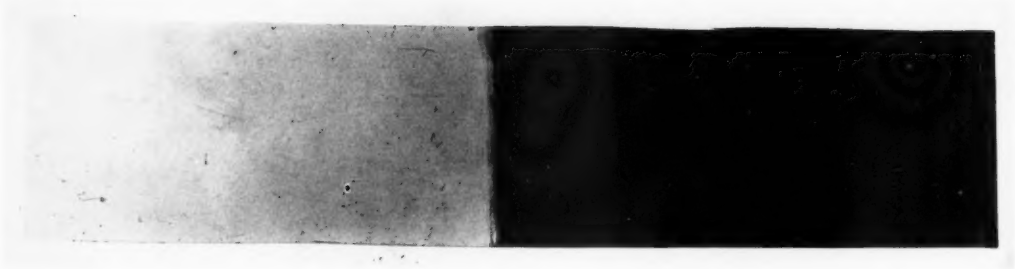


FIG. 3— Cellulose Acetate Sheet, Left-hand Side untreated, Right-hand Side sandpapered. Whole sheet partly saponified, and then dyed with a direct cotton dye

FIG. 4— Unscoured Acetate Fabric partly saponified and then dyed. Weft shows greater degree of saponification than warp

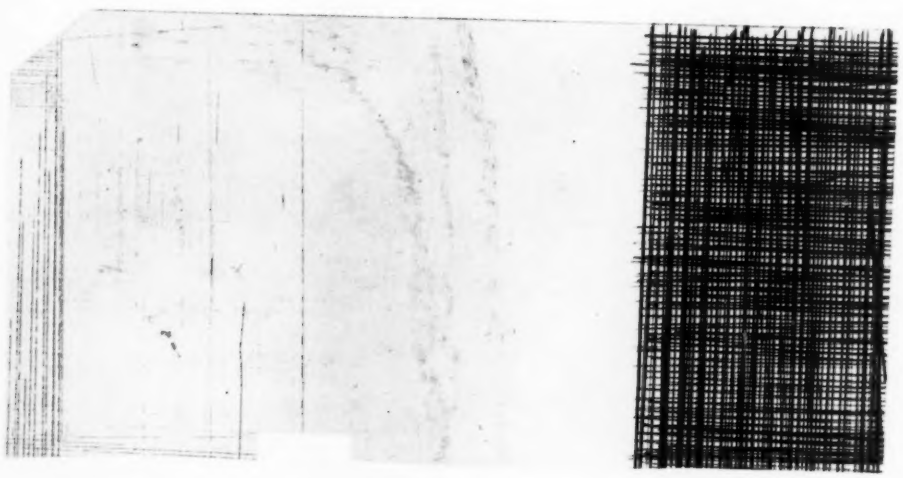


FIG. 5— Cellulose Acetate Film, Left-hand Panel scratched prior to, and Right-hand Panel subsequent to, Boiling Salt Treatment. Whole panel then partly saponified and dyed with direct cotton dyes

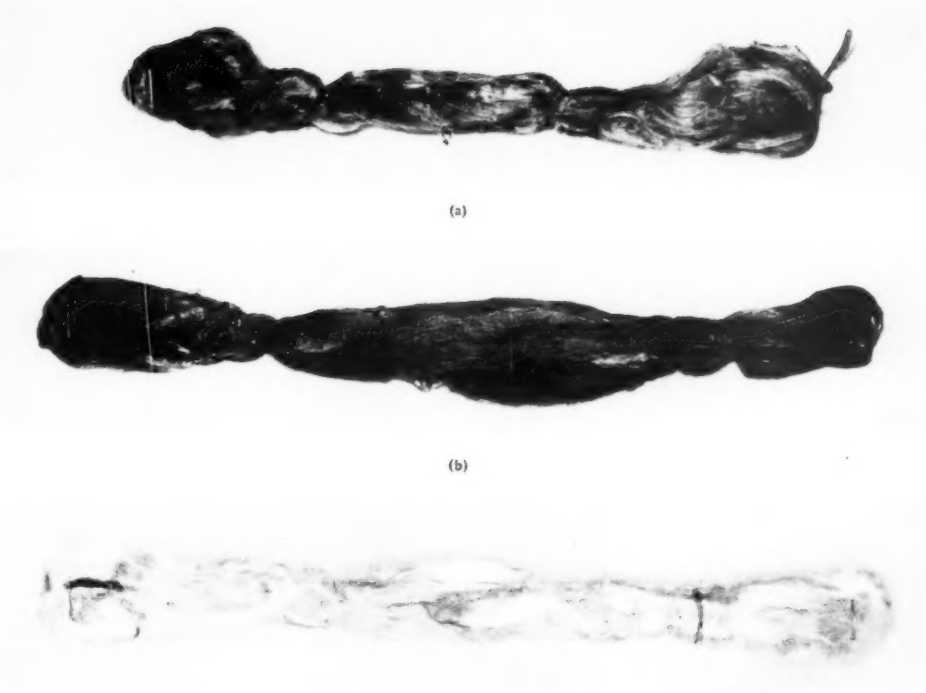


FIG. 6—Cellulose Acetate Yarn—(*a*) Unstretched, (*b*) Stretched 20%, (*c*) Stretched 20% and then treated with 30% Salt Solution at 90°C.—all partly saponified and then dyed with direct cotton dyes

Fig. 7—Cellulose Acetate Yarn stretched until broken, partly saponified, and dyed with direct cotton dyes

FIG. 8—Cellulose Acetate Fabric, Top cut 1 in. and then torn; partly saponified and dyed with direct cotton dyes

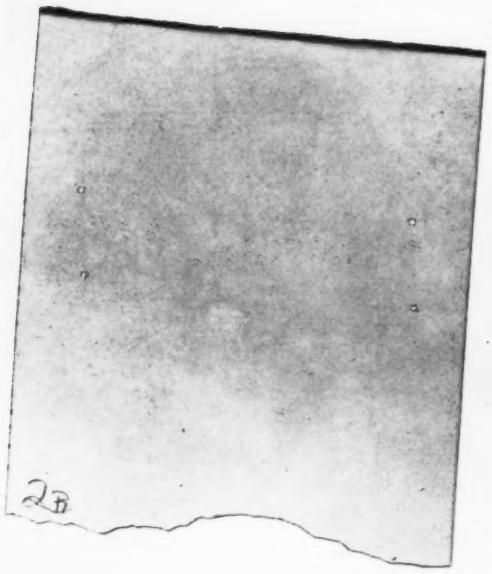
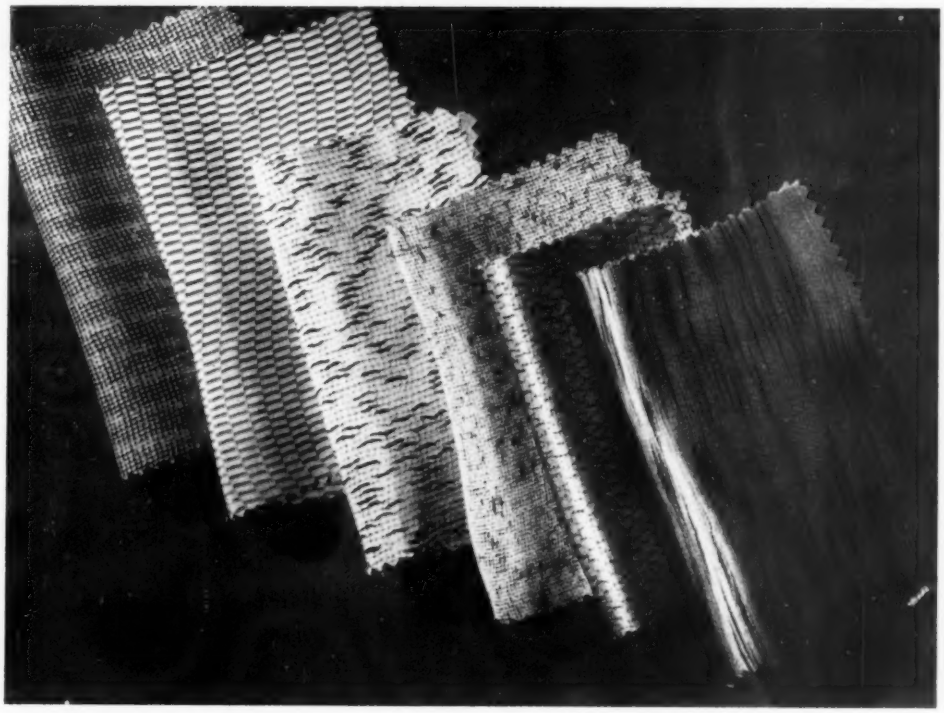


FIG. 9— Cellulose Acetate Film—
Top edge folded until broken
Left-hand edge cut with scissors (note dark spots)
Right-hand edge cut with knife
Bottom edge torn, then partly saponified, and dyed with direct dyes

FIG. 10— Cellulose Acetate Sheet folded tightly and then unfolded; partly saponified and dyed with direct cotton dyes

FIG. 11— Cellulose Acetate Dress Fabric surrounding Small Hole; partly saponified and dyed (× 10)



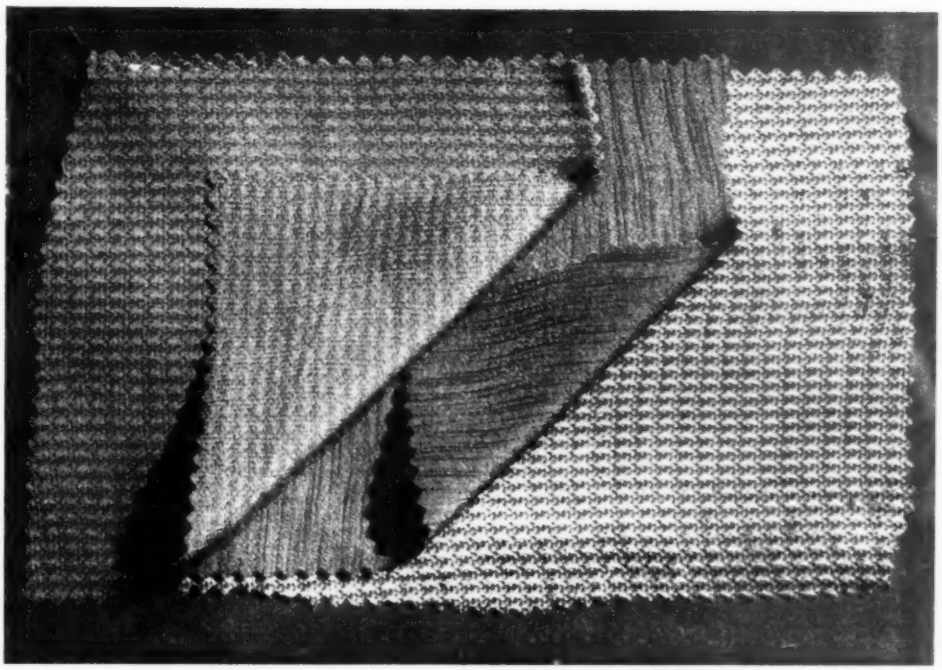


FIG. 12 and 13— Cellulose Acetate Fabrics embossed by Cold Embossing Rollers or by passing between Plain Rollers with other Fabrics; partly saponified and dyed with direct cotton dyes

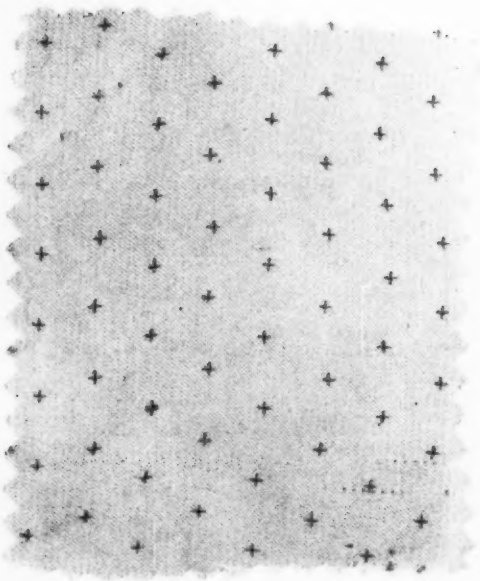


FIG. 14— Cellulose Acetate Fabric embossed by Typewriter Key partly saponified and dyed with solubilised vat dyes

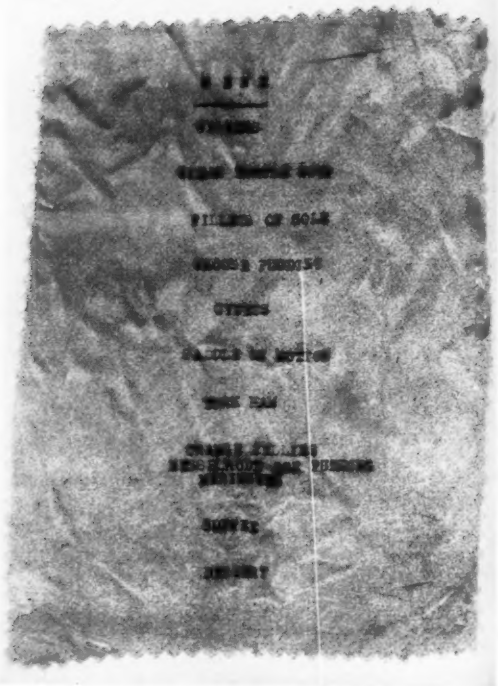


FIG. 15— Worshipful Company of Dyers Menu (pre-war) embossed on Cellulose Acetate Fabric prior to Partial Saponification and Dyeing with direct cotton dyes and dispersed acetate dyes

X-Ray Diffraction Photographs

(CuK_α radiation; distance of specimen from plate 3 cm.)

FIG. 18— Partly Acetylated Bleached Linen Fibres, showing the presence of crystalline native cellulose and triacetyl cellulose I

FIG. 19— Partly Deacetylated Triacetyl Cellulose I, showing the presence of a residual crystalline triacetyl cellulose I along with the reconverted cellulose phase

not possible to lay down a standard time of treatment with caustic soda solution, since this will vary from sample to sample depending upon its origin and history. It may therefore be necessary to carry out one or two critical trials first in order to determine the time required to obtain the optimum difference in effect between the strained and unstrained parts.

Theoretical Speculation

Two phenomena have been reported in this article which may throw a little more light on the surface structure of cellulose acetate fibres and films. Firstly, it has been shown that the rate of saponification is very considerably affected by the physical state of the material. This in broad outline has long been known, e.g. recent work[1] by the Shirley Institute on the differing rates of saponification of secondary cellulose acetate in yarn form and in solution, where also differences in the ease of saponification of various commercial yarns are discussed, differences which have been observed also in the Droylsden laboratories. From the present work it appears that only a very slight change in the physical state is sufficient to change the rate of saponification of fibrous or film cellulose acetate.

Secondly, it has been shown that hot aqueous treatments have the effect of destroying this increased tendency to saponify, and indeed in slowing down the rate of reaction of strained and unstrained material far beyond that of the original material.

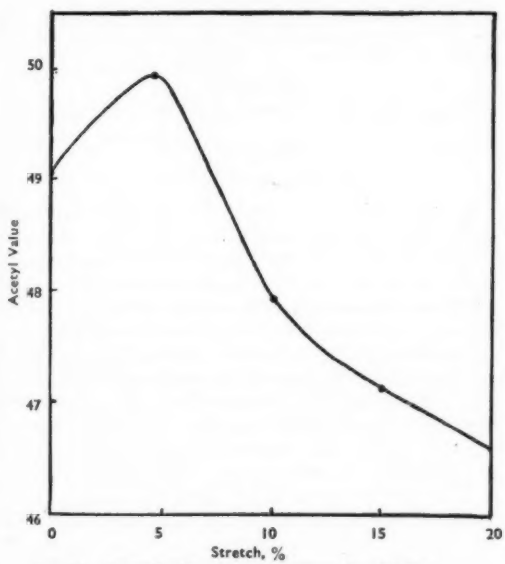


FIG. 16— Saponification–Stretch Diagram for Cellulose Acetate Yarn

During these investigations it has been observed that hot stretching of yarn (during production) reduces the ease of saponification. It is in agreement with accepted theories that saponification is the more rapid the more random and open the structure of the mass. During commercial production of yarns and films there is greater orientation on the surface than in the interior, and the greater the stretch the greater the orientation, therefore the greater the resistance to saponification.

Once the film has cooled, the skin has only limited elasticity and a reconsideration of the variation of degree of saponification with degree of stretch applied to a yarn reveals an analogy with the well known stress–strain diagram for acetate yarn (Fig. 16).

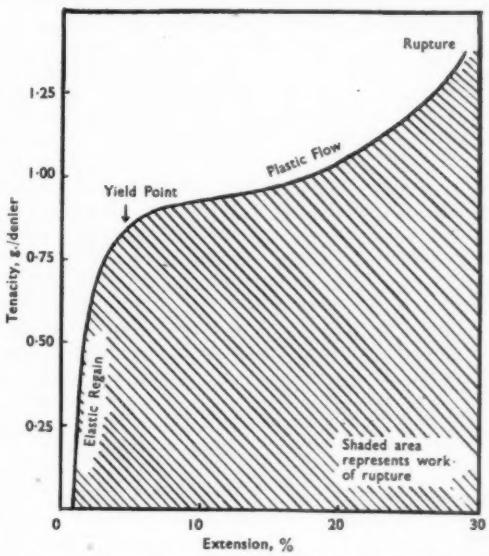


FIG. 17— Stress–Strain Diagram for Cellulose Acetate Yarn

The logical deduction from these two graphs is that in the initial stages of stretching, chain straightening takes place. This tends to tighten up the structure generally and to make saponification less easy; hence the peak in Fig. 16. In further stretching, "plastic flow" takes place with slippage of molecule over molecule, or aggregate over aggregate. This in turn will either expose more reactive groups on the surface, thereby increasing the ease with which saponification takes place; or alternatively, as it were, tear gaps in the surface structure, enabling the alkali to penetrate more readily into the less oriented and more reactive centre of the fibre. It is hoped that cross-sectional photographs will reveal whether by stretching we have increased the rate of saponification at the surface or in the interior.

The behaviour of hot water, hot salt solution, or steam in reducing the tendency to saponify also fits in with these concepts since heat will plasticise the surface, whereby "cracks" will fuse over; or, if the effect of strain is to expose reactive groups, then hot wet treatment will tend to reduce the activity by enabling the structure to relax to a more stable state at a lower energy level.

APPENDIX

Some Notes on the Fundamental Aspects of Differential Saponification

F. HAPPEY

In Coventry we have been carrying out a fundamental study of the processes of esterification and saponification of cellulose, and a few observations on the general trend of this research may throw some light on the results discussed by Mr. Tattersfield. In this work we have been able to show that esterification of cellulose may take place in at least two different ways. Firstly, as in nitration, the esterifying solution may be able to penetrate into the cellulose lattice and so open up the amorphous and crystalline regions and expose the hydroxyl groups of the glucose residues to the reacting liquids. Secondly, penetration of the esterifying solution may proceed only via the intercrystalline and amorphous cellulose, so that in the initial stages of the reaction the crystalline cellulose remains unattacked. This latter reaction is, in the main, typical of the process of acetylation. When the reaction has taken place in these intercrystalline regions, swelling of the triacetate so formed takes place in the reacting liquor, and fresh cellulose surfaces are thereby exposed. Fig. 18 shows the partial acetylation of native cellulose in the fibrous form, and in this X-ray diagram two photographs can be clearly seen, one of triacetyl cellulose I and the other of unchanged native cellulose. Up to an acetyl content of 30% (calculated as acetic acid), no obvious change takes place in the X-ray diagram of the acetylated cellulose. Thus insufficient crystallites of acetyl cellulose are present in the fibre to give a characteristic X-ray diagram of this phase. The acetylation reaction appears to occur mainly in the amorphous and intercrystalline parts of the fibre, up to an acetyl content of 30%.

On saponification (using alkali and triacetate as starting material), a reaction similar in type to the one just described seems to take place. The caustic soda or other saponifying agent used proceeds from the surface of the fibre via the intercrystalline phase, which it can penetrate, to the surface of the crystallites. As the triacetyl glucose residues are transformed into cellulose, these chains are swollen to some extent by the alkali, and the saponification proceeds to the intracrystalline surfaces. Fig. 19 is an X-ray photograph of a partly saponified triacetyl cellulose I which shows the presence of a triacetyl cellulose unattacked by the deacetylating agent along with the cellulose.

In the case of saponification of a secondary acetate, a similar general mechanism of reaction occurs. The easily accessible surfaces react first. On mechanical working, as described by Mr. Tattersfield, the surface of the fibre is disturbed, and it is likely that considerable cracks develop, which can be penetrated by the saponifying agent. These need be only a few angstroms in width to allow penetration of the caustic soda, and they presumably increase in size as the hydroxyl groups replace the acetyl groups in the glucose rings of the cellulose. As it is obviously on these accessible intercrystalline surfaces that the dye molecules are taken up, it is probable that only a small degree of saponification is required in the mass of the fibres to produce hydroxyl-rich areas on which the cotton dye molecules can be adsorbed.

It must, however, be appreciated that the process of saponification is not so clear cut in the case of the secondary acetates, which are not so highly crystalline as are the triacetates, but the same general principle discussed above is probably involved and plays its part in defining the rate at which the initial deacetylation occurs. Thus, in all these cases where the surface is disturbed and broken up, the reaction of saponification proceeds more rapidly. Where, however, surface annealing of the fibres has occurred, then the differential saponification is not so clearly marked between normal and treated fibres.

This discussion does not give a complete picture of the processes involved, but it does in the main set out the general ideas behind the mechanism of acetylation and deacetylation of fibrous cellulose, and gives a clue to the reason why bruising of the surface of the yarn should cause such a difference in the saponification rate. It is probable that a certain degree of intracrystalline penetration occurs in the processes of fibrous acetylation and deacetylation of triacetate, but this is not a major effect. Further, it is not possible to define the limits of the crystalline phase in such a material as a cellulose fibre; and as a detailed discussion of the whole problem is in the course of preparation, any further remarks on the subject would be out of place at this stage.

Reference

[1] Howlett and Martin, *J. Textile Inst.*, **38**, T 212 (April 1947).

Discussion

MANCHESTER SECTION

Dr. F. HOWLETT: Concerning this excellent vindication of the qualitative method, there is a phenomenon which suggests that the effects observed by the Lecturer were due to a microscopic crazing of the surface of the cellulose acetate rather than to any large change in molecular packing.

It was first noticed by Mr. S. Simmens, while at the Manchester College of Technology, that broken filaments of certain textile fibres, but especially of acetate rayon, exhibited a fine dotted appearance running axially and approximately centrally when viewed under the microscope. A more recent study, in conjunction with Mr. Simmens, confirmed the presence of these dots, which probably lie on the cusps of re-entrant sections, but revealed in addition that the surfaces of broken filaments contain a close pattern of small cracks. Both types of crack appear when the yarn is stretched but not broken, and are found also in film which has been cut, bent sharply, or impressed with metal type. Incidentally, the dots were found to be removed from a piece of film by heating in water (although delustring was caused at the same time).

The connection between this effect and the increased diffusion rates found by the Lecturer would seem to be more than coincidental.

A low-magnification electron micrograph of a cast of strained filaments would probably be most informative.

Mr. TATTERSFIELD: We have not been able to detect cracks under the microscope such as those described, but we agree that their presence explains completely the phenomena described. Electron micrographs of casts of strained filaments, preferably with and without a hot salt "annealing" treatment, would be very helpful.

Mr. J. M. PRESTON: It is generally known that any treatment which increases the reactivity of a fibre is equivalent to increasing the accessibility. Increased accessibility shows itself up as increased hygroscopicity (e.g. Hailwood and Horrabin, *Trans. Faraday Soc.*, **42B**, 84 (1946)) and lower density (e.g. Preston and Mhatre, *Internat. Congress of Pure and Appl. Chem.*, London 1947) as well as by increased reactivity. It would therefore be interesting to know if Mr. Tattersfield has found any change of density or moisture uptake resulting from the stretching of his cellulose acetate fibres.

There is one parallel observation to this in the literature: King (*Trans. Faraday Soc.*, **25**, 451 (1929)) reported that wool fibres became more hygroscopic after stretching than before. Further, he reported that if wool fibres were given a permanent setting treatment the hygroscopicity was reduced. It appears that stretching both wool and cellulose acetate fibres whilst dry results in some disruption of the fibre structure, as reported for cellulose fibres by P. H. Hermans (*Kolloid-Z.*, **86**, 107 (1939)), and that this disruption is "healed" by a hot aqueous treatment, at least for wool and cellulose acetate fibres.

Mr. TATTERSFIELD: We regret that we have no information on differences in density or moisture uptake of strained and unstrained acetate yarns or films.

Mr. L. W. PICKUP: Can the Lecturer state the shape of the graph obtained by plotting the acetyl content against time in the saponification of the physically modified acetate? Has the degree of swelling of the modified and unmodified acetates when saponified to the same acetyl content been determined?

Mr. TATTERSFIELD: Graphs of acetyl content against time of saponification have not been prepared for physically modified cellulose acetate, nor have comparative swelling trials been carried out on partly acetylated fibres.

Dr. HAPPEY then made the contribution given as an appendix to the paper.

Mr. J. G. EVANS: The theory advanced by the Lecturer appears on the face of it to be reasonable. The saponification data involve a rate effect which is accelerated by pressure pretreatment of the fibre. This greater accessibility of the fibre suggests an increase in amorphousness, especially as a hot water treatment, which is known to induce greater crystallinity in fibres of this type, nullifies the effect. It would be of interest to know whether the accessibility is increased for molecules other than sodium hydroxide. Does the pressure treatment increase the rate of dyeing with normal dyes or permit dyeing with dyes which do not have affinity for the normal fibre? Secondly, as the pressure is applied perpendicular to the axis, does Dr. Happey find any difference in what Sisson and others have called the "lateral order" of the X-ray fibre diagram?

Mr. TATTERSFIELD: Strained fibres and films saponify more readily than unstrained with caustic alkalis other than caustic soda. Strained fibres and films do not appear to dye more readily with dispersed acetate dyes nor do they acquire an affinity for cotton or wool dyes.

Mr. H. A. TURNER: Was the acetate sheet used in these experiments cast or extruded, or was it cut from the block? If the latter, did the knife marks due to cutting show up on saponification and dyeing? There does not seem to be much evidence of them in the specimens projected on the epidiascope, which is rather surprising, for my experience has been that they are suppressed rather than eliminated by burnishing. For instance, a short exposure to acetone vapour will usually make them reappear.

Dr. Happey has suggested that mechanical strain causes fine cracks in the acetate structure, and that these could account for the increased ease of saponification. He further suggests that boiling in water heals these cracks. Yet delustring with boiling water appears to develop cracks and fissures in the cellulose acetate filaments. Has Mr. Tattersfield carried out any experiments on the rate of saponification of heat-delustred acetate rayon, and if so, with what result?

Mr. TATTERSFIELD: All the experiments have been carried out on extruded film, none on sheet cut from a block.

Whilst no work has been done with heat-delustred acetate rayon, this would be expected to saponify more slowly than the original yarn. Whilst such delustred yarns may have a pitted surface, it is probable that a skin effect will reform in the pits, so that the less oriented core is still protected from the alkali.

SCOTTISH SECTION

Mr. J. A. YOUNG: Has any commercial use been made of saponification applied to yarn dyeing?

Mr. TATTERSFIELD: To the best of my knowledge, saponification methods have not been applied in yarn dyeing.

Mr. T. J. BROWN: Is it possible to pretreat acetate–viscose materials so that in vat dyeing certain evil effects of saponification may be avoided?

Mr. TATTERSFIELD: The present work indicates that a hot salt pretreatment and care to avoid strains after such treatment and before dyeing will obviate some of the uneven results which might occur in the vat dyeing of acetate–viscose fabrics. The ease with which the acetate becomes saponified is also reduced.

Mr. BROWN: The Lecturer has stressed that a cold roller should be used for embossing. What would be the result of using a hot roller? It might be possible to obtain an effect with three depths of

shade by embossing cold, then embossing hot, saponifying, and dyeing.

Mr. TATTERSFIELD: When a hot embossing roller is used, the surface of the fabric or film is softened and a certain amount of "flow" can take place. Therefore, such a roller does not induce strain to the same extent as a cold embossing roller. The result of using a hot roller would be to produce a reduced effect. Regarding the use of hot and cold embossing rollers, it might be more satisfactory to attempt variations in depth by varying the pressure used with cold rollers.

Dr. C. H. GILES: Has this remarkable effect of pressure upon ease of saponification been observed or recorded before?

Mr. TATTERSFIELD: We have not seen any previous references to it. It was only by accident that the observation was made which initiated this present work.

Mr. J. A. LEDDY: Great difficulty has always been experienced in dyeing a solid shade on saponified acetate–cotton mixtures with direct dyes, owing to the saponified acetate taking up the bulk of the dye. Would a pretreatment in boiling salt solution reduce the affinity of the saponified fibre for the dye, thus producing a more solid dyeing? If such is the case, can the Lecturer give any figures as to the strength of salt solution employed for this purpose?

Mr. TATTERSFIELD: The depth of shade obtained on commercially saponified acetate rayon depends on the degree of saponification, which in turn depends on the control of the conditions of saponification. Pretreatment with salt solution will slow down the rate of saponification and thereby give greater control. This, of course, is true only where caustic alkalis are used as the saponifying agents. The treatment is ineffective in the case of soda ash.

The optimum effect appears to be produced with a 20–30% solution of salt, but even hot water reduces considerably the rate of saponification by caustic alkalis. Such pretreatment will also improve the evenness of saponification.

Mr. J. G. B. MCCALLUM: Can the Lecturer advance any explanation for the effect of hot aqueous treatment of physically strained acetate material in eliminating the tendency of these strained portions to preferential saponification?

Further, can the Lecturer assign a reason for the falling off in degree of saponification with strong soda ash solutions of increasing concentrations?

Mr. TATTERSFIELD: The strained parts probably allow more rapid penetration of the alkali to the less oriented or more easily saponifiable core. Hot aqueous treatment softens the skin and allows annealing to take place. It is thought that straining produces minute cracks in the surface of the fibre. When the fibre is softened, these cracks will tend to fill in.

J. T. Marsh, in his book *Mercerising* (London: Chapman & Hall Ltd., 1947, p. 199), suggests that strong solutions of caustic alkali saponify acetate rayon more slowly than do weak solutions because their viscosity prevents them from penetrating to the interior of the fibre. Whilst this explanation may apply also to soda ash solution, the effect may be due rather to the "salt effect" described in the lecture; i.e. the hot soda ash by annealing the surface may reduce the ease with which it can penetrate to the interior.

Mr. R. J. L. SKELTON: Can the Lecturer give any explanation for the warp stripiness which occurs at times on hydrolysed and dyed acetate rayon cloths which have been pretreated in boiling soap solution, and presumably "set"?

Mr. TATTERSFIELD: The causes of warp stripiness are very varied, and do not appear to be fully understood. We agree that hot pretreatment of acetate rayon fabrics, whilst reducing the warp stripiness, by no means removes it. This indicates that the faults are not due primarily to physical strains.

LONDON AND MIDLANDS SECTIONS

Meetings held in the rooms of the Royal Society, Burlington House, Piccadilly, London W.1, on 4th February 1949, Mr. H. A BRASSARD in the chair; and at the King's Head Hotel, Loughborough, on 12th October 1949, Mr. W. L. LANGTON in the chair

The Use of Enclosed Winches in the Dyeing of Rayon Fabrics

D. K. ASHPOLE, R. A. McFARLANE, and C. C. WILCOCK

The possibility of economising in fuel by the use of enclosed winches has long been realised, but as far as is known, there has not been universal adoption of such machines, owing mainly to inconvenient design and the probable lack of appreciation of the amount of fuel which can be saved. A design of enclosure has been developed which has been found serviceable and relatively convenient in use. Experiments are described whereby the fuel saving made possible by enclosure can be calculated. It is shown how to develop the calculations for differing dyehouse conditions. The actual saving obtained, although necessarily only approximate, is compared with the calculated values, and a profit is shown on the first year's working. The effect on dyehouse practice of using such enclosed winches is described. Owing to the higher temperature of dyeing a greater quantity of any bicarbonates present in the water is converted into carbonates, causing the pH of the dye liquor to be increased. Under these conditions certain direct cotton dyes give a different shade compared with open winch dyeing. There is evidence that this is mainly due to the reducing action of viscose in an alkaline dye liquor and to the expulsion of air from the dye liquor. Ammonium sulphate has been found to be effective in preventing the rise in alkalinity of the dye liquor, and an addition of $\frac{1}{16}$% on the volume of the liquor gives the shade normally obtained. Various other effects are described, most of which are to the advantage of enclosure, but some of which necessitate taking special precautions.

(1) Introduction

One of the most important raw materials used by industry is coal. This fact was never more fully realised than during the fuel crisis of 1947, when many works were forced to cease production for a period because at that time coal supplies were insufficient for their requirements.

In the dyeing and finishing trade the coal used for steam-raising purposes has always been a major item of expenditure, and with the steady increase in coal prices over the last ten years has become an increasingly important cost factor. The extent of coal price increases is shown below, where figures are given of the average price per ton of consumable coal at the pit-head—

1938	...	...	17s. 4d.
1939	...	...	17s. 11d.
1947	...	...	40s. 3d.
1948	...	...	47s. 2d.

As the cost of transporting coal has also increased during these years, it is not surprising that much thought has been given to the more economical use of coal in industry.

There are two general ways by which coal can be more economically used by industry, viz.—

(1) By careful control of the burning of coal in the steam-raising plant together with adequate attention to the minimising of heat losses during transmission of the steam to the points of use.

(2) By taking precautions to keep to a minimum heat losses in the machines used for processing, and by the avoidance, as far as possible, of peak demands on steam.

The engineering aspects of these means for economising in the use of coal are well understood and have received considerable attention and publicity from the Ministry of Fuel and Power, who have, amongst their other activities, issued various publications on the subject of fuel economy[1,2].

(2) Enclosed Winch Machines

(a) USE OF ENCLOSED WINCH MACHINES TO SAVE STEAM

It has long been apparent that in the average dyehouse, where large volumes of water are constantly heated to and maintained at high temperatures, the use of enclosed vessels would considerably reduce steam consumption and also reduce the extent of the early morning peak steam load. Enclosed machines have for many years been widely used for the dyeing of yarns, but the adoption of enclosed jiggers and winches for piece dyeing has been far from universal. It is true that many piece dyers have tried out at least one enclosed winch machine, but it is not uncommon to find such machines eventually used as open machines.

(b) DISLIKE OF ENCLOSED WINCHES

A number of reasons have been given for the apparent dislike of enclosed winches, but the major criticisms appear to be concerned with (i) the difficulties of loading and unloading such machines, and (ii) the difficulty of observing the fabric during the dyeing operation, thus leading to fabric damage. Experience with enclosed winches, however, indicates that these objections can to a large extent be attributed to the not uncommon antipathy towards new developments coupled with a lack of perseverance on the part of both the operatives and management to make the use of such machines successful.

(c) SURVEY OF LITERATURE

Whilst there is little evidence of the general adoption of enclosed winch machines, this cannot be ascribed to a general lack of interest in such machines, although information outside patents and manufacturers' literature is somewhat scanty. Thus a survey of the patent literature shows that several enclosed winches of different designs have been patented[3], whilst certain of the machine

makers in Great Britain, e.g. Messrs. Samuel Pegg & Son of Leicester, include enclosed winches in their range. In the United States interest has also been shown in the use of enclosed winches, and although commercial machines are made by a number of firms, including Rodney Hunt Co. of Massachusetts and F. Blickman of New Jersey, the use of such machines is far from general. The position in Canada is similar to that in the United States. Similarly in Germany many forms of enclosed winches have been tried out, most of which have been built by dyeing firms rather than by machinery makers[4]. In Italy enclosed winch machines are made by Mezzera of Milan, and in France by Clermont-Bonte et Fils of Flers-les-Lille and by Liebrecht et Fils of Roubaix.

(*d*) DEVELOPMENT OF TYPE USED AT BOCKING

An impetus to the present investigation of enclosed winches, however, was given by a visit to Sweden by one of us in August 1947. Sweden has for many years been confronted with a shortage of fuel, and sheer necessity has resulted in a very keen appreciation of the need for its economical use. In Swedish dyeing and finishing plants this has resulted in the use of a variety of ingenious means for the recovery of heat from hot waste liquors and gases and, in the plants visited, the almost universal use of both enclosed winches and jiggers[5]. The form of the winch enclosures varied in different plants, but a common factor was that the enclosed winches were used as such and not, as is frequently the case elsewhere, with the doors or windows open.

In the early part of 1947 a conventional type of commercially built enclosed winch machine was installed in the Bocking dyehouse in order to study its advantages and limitations under practical conditions. Experience showed that this machine was difficult to load and unload, and that it had the further disadvantage of having the salting box inside the enclosure, thus making it necessary to open the machine every time additions of dye or salt had to be made. As a result of experience with this machine a hood was built to fit over one of the open winch machines. This hood was of stainless steel with a large area of armour plate glass, and could be completely removed from the winch and lifted out of the way by means of a block and tackle attached to the roof. The salting box had a separate hinged lid to allow additions of dyes or salt without having to remove the complete cover. This enclosed machine gave very good visibility but was clumsy in use. As construction details of one design of enclosed winch were made available by one of the Swedish firms visited in 1947, a second experimental hood was built to this design. The covers used in Sweden were made essentially of a special type of hardboard (compressed wood fibres), but as this material was not available the hood was made of duralumin (an aluminium alloy) with wood supports. Whilst this cover gave encouraging results in practice it was felt that the fabric was not sufficiently visible and that the structure could be reduced in size. This enclosed winch is shown in Fig. 1. Consequently, a further design was constructed, and this, with minor alterations, was the prototype of the covers now in use. This design, constructed of duralumin and armour plate glass, is shown in Fig. 2, 3, and 4.

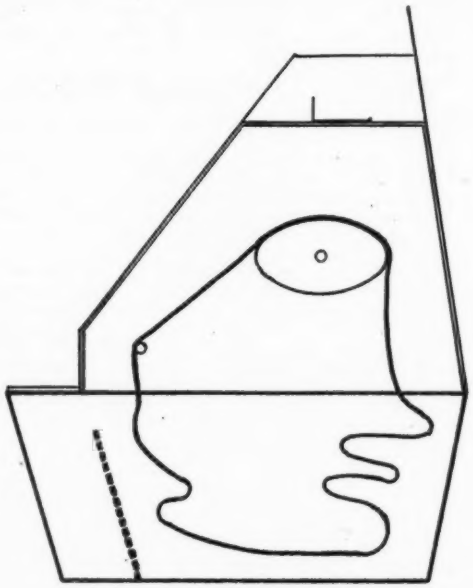


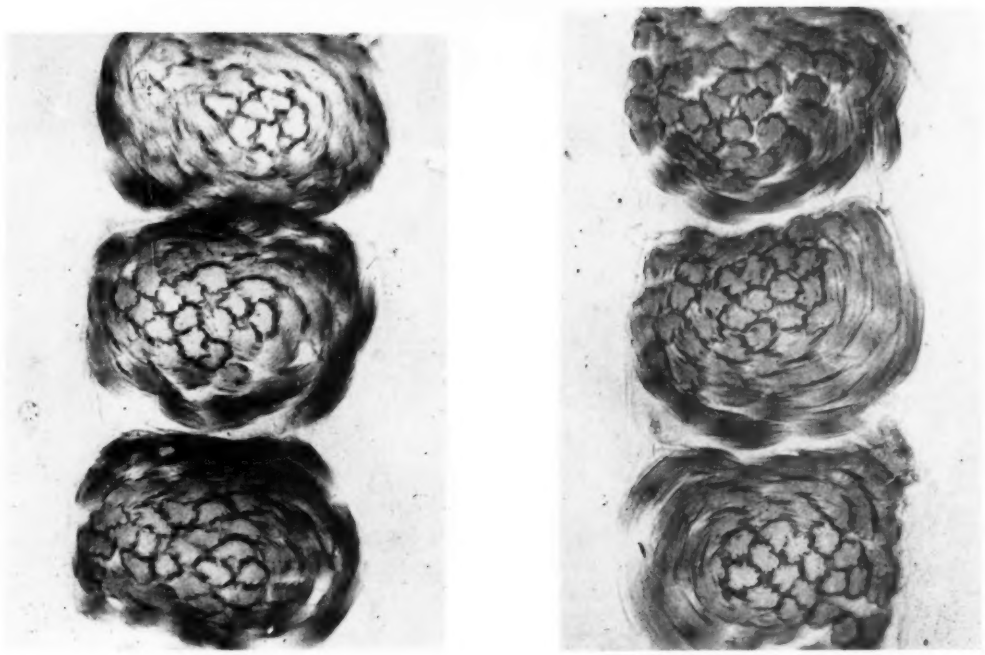
FIG. 4— End View of Enclosure adopted at Bocking

Before using duralumin, consideration was given to the use of stainless steel, but as stainless steel was, and still is, in short supply, it was felt that rather than have to wait for 12–18 months, it was advisable to use the less durable material. The project, which it was desired to carry out quickly, involved the covering of seventy winch machines of varying size, and by using duralumin they were all enclosed in some 4–5 months. Up to the present time the enclosures have been in use for two years. Some have had to receive minor repairs from time to time, but it is estimated that they still have a useful life of 3–5 years.

(3) Estimation of Fuel Economy resulting from the Use of Enclosed Winches

Nowhere in the literature can be found any concrete evidence of the economy in steam which can be effected by the use of enclosed winches under any operating conditions. Various tentative figures have been given, but these values vary considerably among themselves. Thus Fargher[6] quotes "a saving of about 15% in consumption of steam with German-type enclosed winches", whereas much higher estimates than this have been quoted, but without any experimental evidence to support them. Largely owing to the lack of such experimental evidence, the trade has probably not fully realised the amount of saving possible by the use of enclosed winches. It would appear, therefore, that in the past there has been insufficient incentive to enclosure due to lack of reliable information. This attitude should be considerably modified in view of the experimental results which follow.

FIG. 1— Swedish-type Enclosed Winch



(A) (B)

FIG. 11— Penetration of Chlorazol Scarlet GS (ICI) into Crêpe-twisted Weft in (A) Open, (B) Enclosed Winch after dyeing for 1 hr. (× 180)

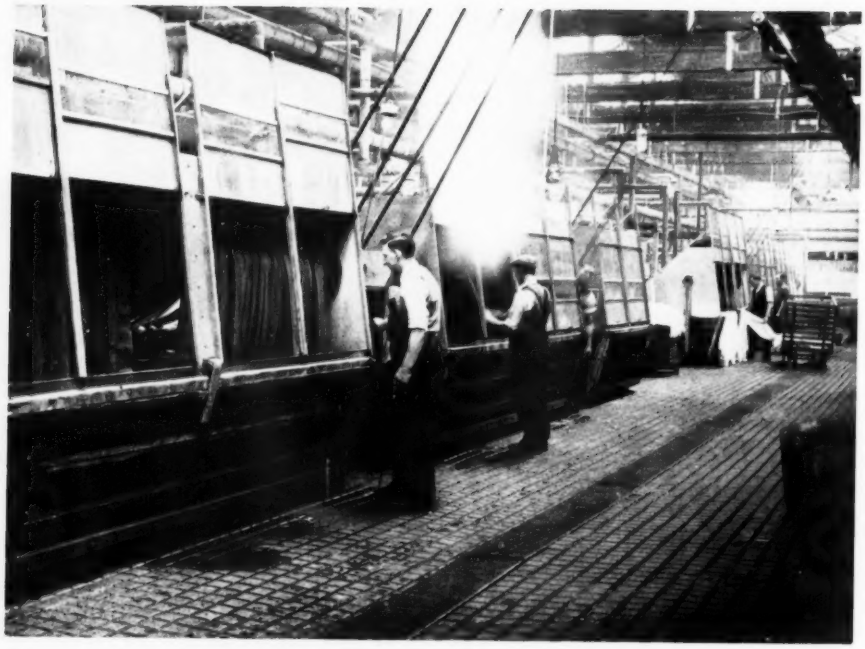


FIG. 2— View of Final Design of Enclosed Winches as installed in Bocking Dyehouse

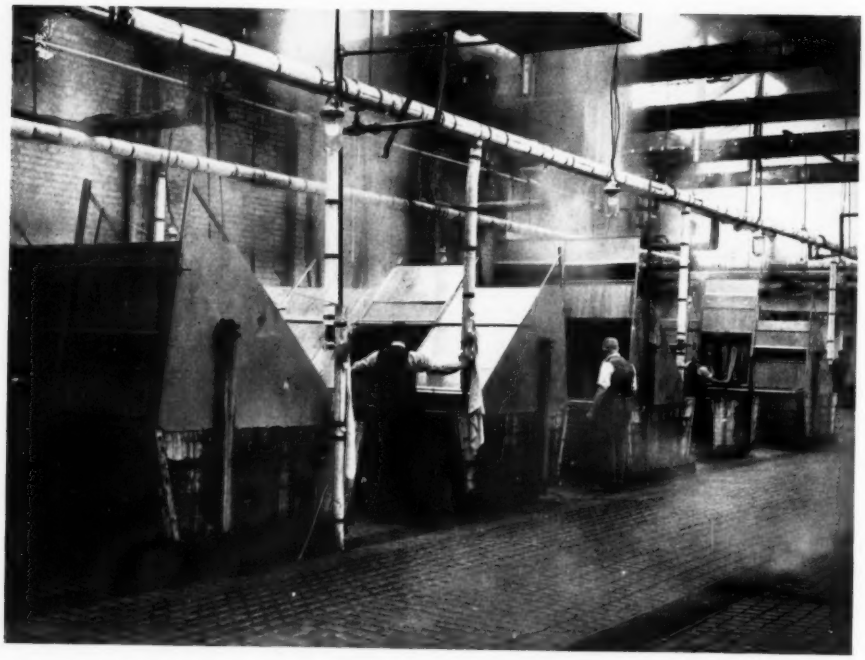


FIG. 3— View of Final Design of Enclosed Winches as installed in Bocking Dyehouse

(*a*) METHOD OF MEASUREMENT

An enclosed winch was fitted with a closed heating coil made from three lengths of 1½ in. internal diameter stainless steel tube each 6 ft. long in place of the normal perforated steam injector. A riser from the bottom of the closed coil led the condensate out of the winch through a steam trap and into a tank of 40 gal. capacity, which could be rapidly emptied by means of a 3-in. valve at the base. An open winch of the same size was selected alongside the enclosed one, and a similar coil, trap, and tank were fitted.

These closed coils considerably retarded the rate of heat input into the winches as compared with the steam injector, and the rate of heating was very much lower. In an initial trial run, it was found that the temperature of the open winch would not rise above 165°F., as the closed coil was incapable of providing sufficient heat. A second coil comprising three lengths of 1½-in. internal diameter copper tube each 6 ft. long was put into the open winch in parallel with the coil already installed, and the condensate run into the common steam trap. With this additional heating it was found possible to reach the "boil". This itself was an indication of the saving possible, since the enclosed winch easily attained the "boil" with the original single closed coil.

The steam consumption was not measured directly, as a suitable steam flow meter was not available. Moreover, such meters are inaccurate unless special precautions are observed, which are not only difficult to achieve, but were impracticable under the working conditions involved. The indirect measure of steam by means of the condensate flow was therefore adopted. This method has the advantage that it is more positive, since a liquid is measured instead of a vapour.

The condensate was collected in the tanks already described, where the amount delivered was ascertained at suitable intervals by means of a dipstick previously calibrated in terms of volume of condensate. When a tank was filled the stopcock at the base was opened until the condensate had emptied, when the stopcock was again closed. The time of emptying was noted, so that allowance could be made for the small amount of unmeasured condensate delivered during the emptying period. The stopcock was sufficiently large to allow the condensate to escape rapidly, and the time of emptying was small compared with the total time; hence the allowance necessary was only small (approx. 5% of the total).

Owing to the heating coil capacity of the open winch being greater than that of the enclosed winch (made necessary by the higher steam consumption of the former at high temperatures), the open winch would have initially heated more quickly than the enclosed winch. The steam inlet valves were therefore controlled manually in order to keep the temperatures of the two becks in step with each other. Initially it was necessary to throttle down the steam to the open winch, but as the temperature rose the vapour loss increased and the steam flow had to be increased for the temperature rise to keep in step with the enclosed winch. The temperatures were measured by means of thermometers immersed in the salting box, and the liquor was thoroughly stirred with a paddle before taking the readings.

(*b*) EXPERIMENTAL RESULTS

(i) *High-temperature Dyeing*

A direct comparison of the open and enclosed winches was made whilst making two dyeings under works conditions, both nominally at the boil.

Each winch was filled with 410 gal. of cold water, and 225 lb. of a viscose–acetate fabric in the form of ten ropes, each approx. 100 yd. in length, was put in each beck. Both jobs were dyed to the same shade. The figures (to the nearest 100 lb.) obtained in this test are shown in Table I.

TABLE I

Comparative Amounts of Steam used in Open and Enclosed Winches dyeing at High Temperature under Experimental Conditions

Period	Time taken (hr.)	Steam used (lb.) Open	Enclosed	Difference
Heating ...	2	1100	700	400
Dyeing ...	5	2300	600	1700
Total	7	3400	1300	2100

The open winch was only "boiled" gently with steam rising in bubbles through the liquor, and the average temperature at the front of the winch during the dyeing was 195–200°F. The temperature at the back of the winch was some 10°F. less than at the front, owing to the fabric becoming cooled during its passage through the air and down into the back of the winch.

The enclosed-winch liquor temperature was kept slightly above the open winch to make sure that the figures of savings obtained were not artificially large and impossible to obtain under normal working conditions. The average temperature at the front of the winch was 200–205°F., and at the back of the winch less than 1°F. lower.

(ii) *Low-temperature Dyeing*

A similar comparison was made between the open and enclosed winches when dyeing at a low temperature (150°F.), such as may be used for dyeing bright acetate mixture fabrics.

To each winch was added 425 gal. of cold water and 180 lb. of fabric comprising seven ropes each of approx. 100 yd. The figures (to the nearest 10 lb.) obtained in this test are shown in Table II.

TABLE II

Comparative Amounts of Steam used in Open and Enclosed Winches dyeing at Low Temperature under Experimental Conditions

Period	Time taken (hr.)	Steam used (lb.) Open	Enclosed	Difference
Heating ...	1¼	440	410	30
Dyeing ...	4¼	650	140	510
Total	5½	1090	550	540

After the initial heating up both winches were maintained at a temperature of 150 ± 2°F.

(*c*) CALCULATED FUEL SAVINGS ON ABOVE DYEINGS

The high-temperature comparative dyeings showed a total saving of 2100 lb. of steam, whilst the low-temperature comparative dyeings showed a total saving of 540 lb. of steam, per dyeing. Taking

figures of 6 lb. of steam generated per lb. of coal burnt and the steam cost at $\frac{1}{20}$d. per lb., the savings on these two dyeings are shown in Table III.

TABLE III

Direct Savings on Two Experimental Dyeings due to Enclosure

Temperature	Saving Coal (lb.)	Direct Cost
High (200°F.)	350	8s. 9d.
Low (150°F.)	90	2s. 3d.

On the basis of only one dyeing per day, the annual savings would be £110 or 40 tons of coal per winch at the high temperature, and £27 or 10 tons of coal per winch at the low temperature.

(*d*) CALCULATED FUEL SAVINGS FOR DIFFERENT CONDITIONS

The figures of savings calculated above apply to only one set of conditions, which will not necessarily be the same for the whole of a dyehouse on normal production. A number of other factors have to be taken into consideration if the estimate of the saving possible per winch averaged over the dyehouse is to be accurate.

These separate factors are listed below and discussed in relation to the effect that they had on the dyehouse under consideration. In other dyehouses the same factors will enter into the estimate, but their relative importance may be entirely different.

(i) *Dyeing Temperature*

The test figures given in Table III relate to two entirely arbitrary temperatures, and even if they are the only two involved, we at least need to know the relative numbers of dyeings which are carried out at the respective temperatures. In general, however, unless thermostatic control of the winches is employed (and this is difficult with open winches at temperatures anywhere near the boil), the temperatures of the dye liquor will vary throughout the dyehouse, depending on the individual dyer in charge.

Two determinations were therefore made, namely (*A*) of the rates of loss of heat from open and enclosed winches at different temperatures, and (*B*) of the distribution of dyeing temperatures throughout the dyehouse.

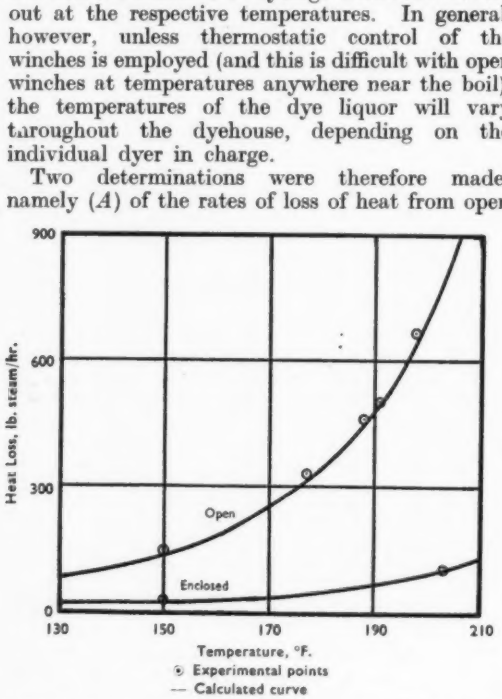


FIG. 5— Variation of Heat Loss from Open and Enclosed Winches with Temperature

The former (*A*) were determined by direct measurement at several temperatures, and the values obtained compared with a theoretical curve calculated from data by Goldstern[7] on vapour loss (which will comprise the bulk of the heat wasted). The agreement was well within experimental error (Fig. 5).

The latter (*B*) was obtained by making a survey of the temperatures of all open winches in the dyehouse when dyeing was taking place. The temperature was measured in the salting box, and since the back of the winch was at a lower temperature than the front, the mean temperature of the evaporative surface would be lower than the values given.

The frequency distribution of the temperatures obtained (smoothed by taking running means of seven consecutive temperatures in order to compensate for the small number of readings taken) is reproduced in Fig. 6.

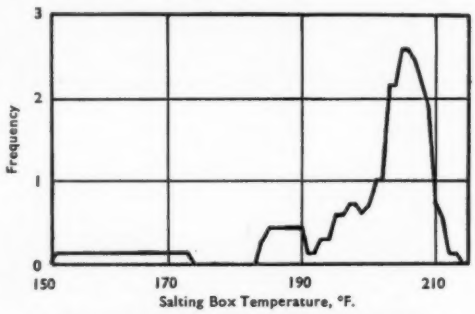


FIG. 6— Distribution of Dyebath Temperatures before Enclosure of Winches

It is obvious that a calculation of the arithmetic mean of the salting box temperature followed by a reading of the corresponding steam wastage from Fig. 5 will give a serious underestimate, owing to the increasing steepness of the curve for the open winch as the temperature approaches the boiling point. A true value is obtained by reading off from Fig. 5 the steam wastage corresponding to each individual temperature and averaging these figures. The weighted averages so obtained are 650 lb./hr. for the open and 120 lb./hr. for the enclosed winch.

(ii) *Method of Heating*

The tests were carried out with closed-coil heating to facilitate measurement of the steam consumption. In works practice an open-coil steam injector is used for heating, and the time required to reach the dyeing temperature is very much less than with the closed coil. The steam savings obtained in reaching the dyeing temperature will be smaller, owing to the shorter time during which the vapour loss can take place. In fact, the difference in steam consumption between the open and enclosed winches in reaching the boil is small compared with that obtained during dyeing at the "boil". An estimate is best obtained by heating

two adjacent winches (one open, one closed) containing similar amounts of water and identical steam injectors with the steam valves full open, and timing how long each takes to reach the boil. The open winch is found to take about 10% longer than the enclosed. The steam consumed in heating the enclosed winch will not be appreciably different from that calculated from theory. Thus 620 lb. of steam is needed to heat the enclosed winch, and 700 lb. to heat the open winch, to the high temperature.

During the dyeing at temperatures close to the boil, the steam injector will be less efficient than the closed coil owing to the fact that not all the steam injected is condensed in the liquor but much of it rises to the surface as bubbles. This effect will vary with the design of the steam injector and its position in the winch. For the dyehouse under consideration this loss amounted to about 20% under the conditions used. Hence rates of steam consumption are amended from 650 to 800 lb./hr. for the open, and from 120 to 150 lb./hr. for the enclosed, winch whilst dyeing at a high temperature.

(iii) *Average Dyeing Time*

The dyeing times in the tests were the times required to dye the goods to the correct shade with sufficient penetration. For different types of goods this dyeing time will obviously vary very considerably. A dyeing of a standard shade on a loosely woven light-weight fabric can be accomplished in well under an hour, whereas dyeing a very dark or black colour on to a tightly woven, highly twisted, heavy-weight crêpe fabric might well take over eight hours to secure sufficient penetration.

The average dyeing time of the dyehouse at the period of this investigation was estimated at approx. 4 hr.

(iv) *Amount of Fabric dyed*

The vapour loss from a standard 10 end winch when dyeing only 5 ends will not be reduced proportionately and an allowance has to be made if the winches are not customarily filled to their standard capacity. This was unnecessary in the case considered.

(v) *Number of Dyeings per Day*

When the average time of dyeing is lower, a greater average number of dyeings would be expected per day, unless a greater time was spent in preparatory process in the winch or otherwise. Hence the multiplying factor from savings per dyeing to savings per annum will be bigger for shorter average dyeing times.

(vi) *Overall Savings*

The final comparison data sheet calculated for an individual dyeing using steam injectors is shown in Table IV.

TABLE IV

Comparative Amounts of Steam used in Open and Enclosed Winches calculated for Average Dyehouse Conditions at Bocking

Period	Time taken (hr.)	Steam used (lb.) Open	Enclosed	Difference
Heating ...	½	700	620	80
Dyeing ...	4	3200	600	2600
Total	4½	3900	1220	2680

With 4½ hr. total time in the winch and a 9-hr. working day (allowing 1 hr. for loading and preparation and 1 hr. for washing, softening (where necessary), etc., and unloading) a maximum of 300 dyeings per winch per year will be attained (allowing for additional time where dyeings have to be discontinued at the end of the day and restarted from cold the following morning).

Thus the total savings estimated correspond to 60 *tons of coal and* £170 *per ten-rope winch per annum.*

(*e*) DISCUSSION OF RESULTS

(i) *Percentage Savings*

The figures given above are the direct savings per ten-rope winch per annum for a particular set of conditions. No attempt has been made to express these results in terms of a percentage saving, as has often been done. This is largely because the percentage saving can be very misleading; indeed it cannot mean anything when it is separated from the dyeing conditions to which it applies.

As an example, let us consider a simple case where an open and an enclosed winch both take

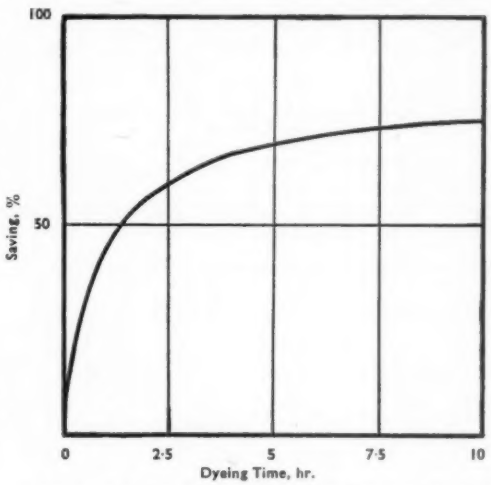


FIG. 7— Variation of Percentage Saving (due to enclosure) with Dyeing Time

700 lb. of steam to heat, but where the former uses 800 lb./hr. and the latter 150 lb./hr. at the boil. Then for different dyeing times the percentage steam savings are given by the curve in Fig. 7.

It will be seen that for a dyeing time of 2 hr. the saving is 57%, whilst for a dyeing time of 4 hr. the saving is 67%, an increase of only 10% for a doubling of dyeing time.

The actual savings in fuel and cost per dyeing will be double for the 4-hr. dyeing compared with the 2-hr. dyeing when both are enclosed.

It is clearly impossible to claim that any one design of enclosure will save a given percentage of steam. In fact, the actual design of enclosure from the economy viewpoint is less important than the conditions of use when arriving at a figure of percentage saving.

(ii) *Direct Savings*

The figures of direct savings per dyeing with the dyeing conditions carefully specified are much more useful criteria for assessment of overall savings. Where the conditions are different from those specified, the values of savings generally can be calculated by direct proportion. Thus in the simple case cited in section (*a*) above, the direct saving can be obtained from Fig. 8.

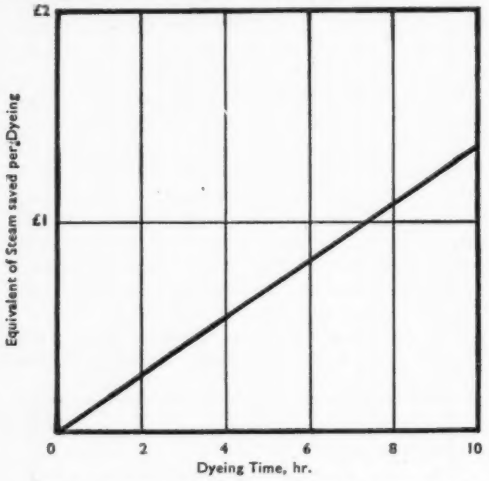


FIG. 8—Variation of Direct Saving (due to enclosure) with Dyeing Time

If a comparison is desired between the open and enclosed winches as opposed to an individual direct value, then the extent of the true savings is better realised from Fig. 9 than from Fig. 7.

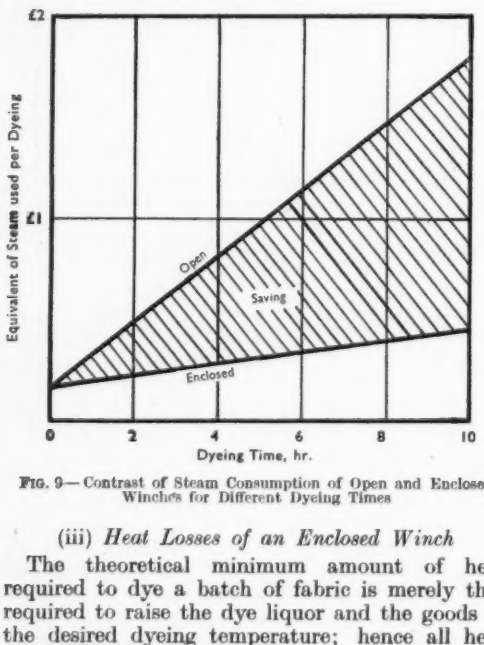


FIG. 9—Contrast of Steam Consumption of Open and Enclosed Winches for Different Dyeing Times

(iii) *Heat Losses of an Enclosed Winch*

The theoretical minimum amount of heat required to dye a batch of fabric is merely that required to raise the dye liquor and the goods to the desired dyeing temperature; hence all heat supplied after reaching this temperature is wasted heat, and if the machine could be completely insulated thermally, the wastage of heat would be eliminated.

This wastage of heat is cut down to a mere fraction of its former value by enclosure, which reduces the vapour loss. The question then arises as to whether heat losses can be reduced further by other means such as lagging the metal enclosure.

The total heat loss from the final design of a ten-rope enclosed winch at the boil is estimated at 150 lb. of steam per hour.

Calculations of the total conducted, convected, and radiated heat losses from the exposed surface of the winch (these come only from the surface presented by the hood, as the beck itself comprises a stainless steel liner in a 3 in. thick solid pine frame, providing adequate thermal insulation) give a value equivalent to 60–70 lb. of steam per hour.

Hence more than half the heat wasted in an enclosed winch is still due to vapour loss. The extent of this vapour loss has been found to depend more on the dyer in charge of the machine than on the design of the cover itself, since the same amount of vapour will escape from much smaller holes and crevices if the dyebath temperature is raised only a fraction of a degree.

(iv) *Fuel Savings achieved in Practice*

The fuel savings achieved as a result of the enclosure of winches can ultimately be assessed only from the effect at the boiler-house. Unfortunately this is complicated, as many factors enter into the amount of coal consumed. Probably the best estimate for comparison purposes is the amount of steam used per pound of fabric dyed, since this cuts out two of the variables, viz. the calorific value of the coal and the boiler-house efficiency.

One obvious difficulty arises in that the steam used is the total for the whole factory and not just that used in dyeing; thus the saving is to some considerable degree masked by the rest of the works continuing as before. Another serious difficulty is that the production in this particular factory was increasing before, during, and after the changeover, so that no strict comparison on equal production is possible. This production increase in itself will tend to reduce the amount of steam used per pound of goods dyed, since the steam overheads (week-ends, standing losses, etc.) become proportionately smaller. The extent of this reduction is, however, somewhat uncertain.

Hence it is obvious that assessments of savings based on boiler-house figures can hope to be only very approximate, and must not be relied on to give more than the order of the total fuel saving.

The figures obtained from boiler-house records show that a reduction of about 7 lb. of steam per lb. of fabric dyed was obtained after enclosure of winches. Taking a boiler-house production of 6 lb. of steam generated per lb. of coal burnt and the price of coal delivered to the factory as 65s. 0d. per ton, then the saving will be—

$$\frac{7}{6} \times 65 \times \frac{12}{2240} \simeq 0{\cdot}4\text{d. per lb. of fabric dyed}$$

If we now assume a production of 70,000 lb. of fabric dyed per week, the annual saving will be—

$$£\frac{0{\cdot}4 \times 70{,}000 \times 50}{240} \quad £6000 \text{ per annum}$$

The order of this result agrees substantially with the value calculated from the experiments described, and it would be difficult—if not impossible—to obtain a much better estimate.

It should be noted at this juncture that the total cost of making and fitting the enclosures was £2500, so that even in the first year's working a financial saving can be shown as well as a fuel economy.

(v) *Increased Production*

Owing to the fuel savings effected by means of enclosure, it has been found possible to increase production out of proportion to the increase in coal consumption. This large increase in production would have been impossible with open winches, as the demand on the boilers would have been beyond their peak capacity.

The fluctuations in steam demand are made greater as a result of enclosure, because the difference between the demands of heating and maintaining the temperature are very much larger, as has been pointed out by Goldstern[7]. The complete answer to this difficulty is the steam accumulator, but a satisfactory compromise has been reached by some staggering of heating-up times. This has been arranged so as to cut down rather than increase standing time by employing men to start early and heat the liquor of all available winches to the dyeing temperature before the main load of the rest of the factory is added. This effectively spreads and reduces the early morning peak load on the boilers to a reasonable value.

(4) Effect on Dyehouse Practice of using Enclosed Winches

(*a*) DIRECT COTTON DYES

It was observed during bulk dyeing that a number of direct cotton dyes did not give their true shade, and that certain of them used for flattening purposes did not have the desired effect. It was realised that this might be due to one or more of a number of possible causes, including the reducing action of viscose in the presence of alkali[8] and hydrolysis of the dye in alkaline baths.

One of the effects of the higher temperature of dyeing obtained in an enclosed winch as compared with an open winch is that a greater quantity of any bicarbonate present in the water is converted into carbonate. Using Bocking water (an analysis is given in Table V), the result of this chemical action is to raise the pH of the water from 7–8 to 10–11. Under the conditions of enclosed winch dyeing, a number of direct dyes are destroyed or give a different shade from the one obtained in an open winch

TABLE V

Analysis of Bocking Water

DIRECT FROM ARTESIAN WELL	Parts per 100,000
Total solids	60·0
Calcium (Ca^{++})	8·5
Magnesium (Mg^{++})	3·0
Chloride (Cl^-)	11·5
Sulphate (SO_4^{--})	6·5
Temporary hardness (as $CaCO_3$)	30·0
Permanent hardness (as $CaCO_3$)...	4·0
Free carbon dioxide (CO_2) ...	0·2
pH 7·3	
AFTER SOFTENING	
Total hardness	0·5–1·0
pH 7·8	

It has been found that an effective method of countering this effect is to make an addition of ammonium sulphate to the dye liquor before commencing dyeing. The amount required will vary according to the particular water, but with Bocking water an addition of $\frac{1}{16}$% on the volume of the dye liquor was effective in countering the pH rise. It is preferable to make the addition of ammonium sulphate at the beginning of the dyeing, i.e. before raising the temperature, owing to its relatively rapid dissociation at high temperatures, and its "salting on" effect on direct dyes. Further, it is preferable to prevent rather than correct any increase in the pH of the dye liquor. By employing a blank liquor and plotting pH against time, an indication has been obtained that the breakdown of ammonium sulphate to give ammonia and sulphuric acid is not spontaneous (Fig. 10).

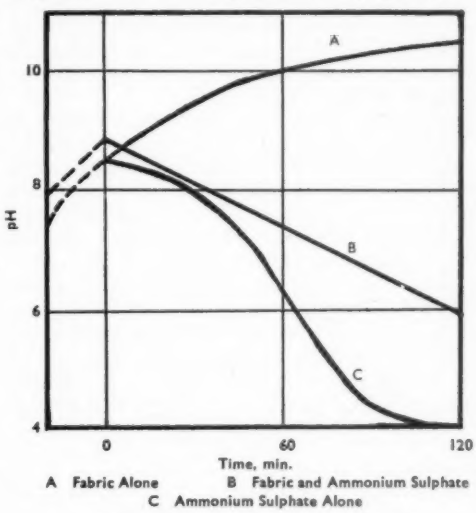


FIG. 10—Change of pH in Closed Dyepot

The primary reaction may be—

$$(NH_4)_2SO_4 + NaHCO_3 \rightarrow Na^+ + NH_4^+ + SO_4^{--} + H_2O + NH_3 + CO_2$$

The partial loss on boiling of the last two components would explain the slow reduction in alkalinity, and is in general agreement with the pH values observed. The equation implies that an excess of ammonium sulphate over the quantity required to convert the bicarbonate to sodium sulphate is necessary to produce a slightly acid dyebath; this agrees with practice, where an addition of approximately one molecular proportion of ammonium sulphate is required for each molecular proportion of dissolved bicarbonate.

Other compounds have been tried to counter the pH rise and subsequent breakdown of dyes, but none has been found to be as effective or convenient to use as ammonium sulphate. Examples are—acetic acid, aluminium sulphate, ammonium dihydrogen phosphate, ammonium thiocyanate, Calgon (Albright & Wilson), sodium dihydrogen phosphate, sodium chlorate and acetic acid, sodium

perborate and acetic acid, and sulphuric acid. Both acetic acid and sulphuric acid may be used if added in sufficient quantity, but they are less desirable additions to a dye liquor than is ammonium sulphate.

A study of the breakdown of dyes at the higher temperatures obtained in enclosed winch dyeing has been made, but in this paper it is intended to give only more general results.

It has been established that in the enclosed winch no significant increase above atmospheric pressure is obtained and that from a dyeing point of view the main advantage of enclosure lies in maintaining a uniform high temperature throughout the beck. An attempt was made to imitate these conditions in the laboratory by using conical dyepots fitted with watchglass covers. A small piece of lead was placed on top of the watchglass cover in order to keep it in place. Later more effective control was obtained under reproducible conditions by fitting stainless steel tops on to bottles. The weight of the tops was such as to prevent any appreciable amount of steam escaping during dyeing without significantly increasing the pressure inside the bottles. Dyeings were carried out in the bottles, which were uniformly heated in an oil-bath thermostat regulated to $\pm 0{\cdot}25$°c.

Experiments carried out under the conditions described indicated that the temperature of the breakdown of dyes was of the order of 99–100°c. Experiments carried out at significantly lower temperatures for various lengths of time have failed to produce the effect. This indicates that the boiling action (ebullition) as distinct from temperature, with accompanying expulsion of air and agitation of the liquor, may be a factor. It has been demonstrated that one of the main factors in the breakdown is the increased alkalinity of the dyebath, but it is significant that the breakdown does not occur at 99–100°c. if no fabric is present, even if further alkali is added. Only a slight change of shade is obtained if carefully scoured cotton is used in place of viscose, but a bigger change is obtained if the cotton has been bleached. It is apparent, therefore, that the breakdown is not a case of direct hydrolysis, and that, at least at first, the reaction is probably one of alkaline reduction. A further point is that, if sulphur is present as an impurity in the viscose yarn, the breakdown takes place more quickly.

Over forty dyes were examined under the conditions described, using a carefully scoured Fibro fabric, 2% dye on the weight of the fabric, 40 : 1 liquor : fabric ratio, and with the addition of 10% salt on the weight of the fabric. Bocking softened water was employed throughout. Sixteen of the dyes were found to break down or give off-shades when viscose was dyed under enclosed conditions in the absence of ammonium sulphate. These dyes were—

Diazo Indigo Blue BR (CAC) (*C.I.* 316)
Durazol Blue GS (ICI)
Durazol Blue 4GS (ICI)
Chlorantine Fast Blue 8G (CAC)
Diphenyl Fast Blue 4GL (Gy)
Durazol Blue 3RS (ICI)
Diphenyl Blue M 4932 (Gy)
Chloramine Navy Blue L (S)
Diphenyl Fast Blue Green BL (Gy)
Chlorantine Fast Green BLL (CAC)
Chlorazol Green GS (ICI) (*C.I.* 594)
Diazo Fast Green GL (CAC)
Viscose Blue Grey NB (CN)
Durazol Grey BS (ICI)
Durazol Grey RGS (ICI)
Carbide Black Z 2629 (CAC)

It is interesting to note that the sixteen dyes are all blues or greens, or mixtures containing a blue or green. The length of time of dyeing required to obtain a significant breakdown varies from dye to dye. Under the laboratory conditions described some dyes show a significant change in an hour, whilst others take more than two hours.

Two dyes whose chemical constitutions are known[10], namely Chlorantine Fast Blue 8G and Chlorantine Fast Green BLL, have been studied in detail. It was found that the breakdown proceeded in stages. In the case of the green dye the breakdown in the presence of viscose was allowed to take place for 45 min., the viscose was then removed, the bath made acid, and a piece of wool introduced into the bath. The wool was dyed a deep red. The experiment was repeated, but the breakdown was allowed to proceed further, for 240 min., before removing the viscose. In this case the wool was dyed a deep yellow. The experiment was again repeated, the breakdown being allowed to proceed still further, for 360 min., before removing the viscose. The wool was dyed a pale yellow. Similarly the blue dye was found to dye wool two shades from acidified dye liquors in different stages of breakdown. On examining the dyed wool fabrics it was found that the dyes had the properties of acid dyes; e.g. they were stripped with ammonia and Glauber's salt and redyed on addition of acid.

Taking into account the original chemical structure of both dyes, an indication is obtained from these experiments that these dyes lose their original substantivity for cellulose fibres primarily by reason of breakdown of the chromophoric azo groups under the conditions of enclosed dyeing due to alkaline reduction, although some hydrolysis of the side chains may possibly also take place at a later stage.

A detailed study of the breakdown of the two dyes is being made in the laboratory.

A number of direct cotton dyes are substantially unaltered and give the normal shade when used for dyeing viscose in an enclosed winch or under the laboratory conditions already described. Examples of some of these dyes are—

Chlorazol Fast Pink BKS (ICI) (*C.I.* 353)
Durazol Red 2BS (ICI) (*C.I.* 278)
Durazol Red 6BS (ICI)
Chlorazol Fast Scarlet 8BS (ICI) (*C.I.* 326)
Chlorazol Fast Scarlet GS (ICI)
Direct Fast Scarlet 8E (CAC) (*C.I.* 327)
Rosanthrene Fast Bordeaux 2BL (CAC)
Benzanil Fast Bordeaux 2BLN (YDC)
Diazol Bordeaux NRM (CN)
Pyralon Orange G (LBH) (*C.I.* 653)
Direct Fast Orange 8E (CAC) (*C.I.* 326)
Durazol Yellow 6GS (ICI)
Durazol Yellow 3RS (ICI)
Chlorantine Fast Yellow 8L (CAC)
Chlorantine Fast Green 5GLL (CAC)
Chloramine New Blue 5B (S)
Melanthrene BH (CAC) (*C.I.* 401)
Durazol Blue 2GNS (ICI)
Durazol Blue 4RS (ICI)
Durazol Helio BS (ICI) (*C.I.* 319)
Chlorazol Fast Helio 2RKS (ICI) (*C.I.* 319)
Durazol Violet 2BS (ICI)
Diphenyl Brown BBN (Gy)
Diphenyl Brown FY (Gy)
Chlorazol Black A2BN (ICI)

(*b*) RATE OF DYEING—EXHAUSTION

Comparative dyeing trials were carried out in the laboratory at 90°C. under open and enclosed conditions and at 100°C. under enclosed conditions. The dyeings were carried out for a fixed period of time employing a constant salt concentration and liquor : fabric ratio. Under these conditions there was a marked increase in the rate of exhaustion at 99–100°C. compared with dyeings carried out at 90°C. The increase was not the same for all dyes, but generally was of the order of 5–10% greater at identical intervals of time where equilibrium had not been reached. The time to reach equilibrium was shortened in all cases examined, although the equilibrium values were different, those at the higher temperature being slightly lower.

The effect of adding ammonium sulphate for the purpose of countering the increase in pH of the dye liquor has been found in most cases to have little effect on the time of exhaustion at 90°C., allowing for increase in rate of exhaustion due to added electrolyte. In some cases, e.g. Diazo Fast Green GL and Diphenyl Fast Blue Green BL, the lowering of the pH (due to addition of ammonium sulphate) reduced the rate of exhaustion to an appreciable extent. No comparative tests have been made at 99–100°C. owing to the change of shade obtained without the addition of ammonium sulphate.

(*c*) PENETRATION OF DYES INTO THE YARN

In the dyehouse in question a large number of fabrics made from highly twisted yarns, such as crêpe fabrics, have been dyed in open and in enclosed winches. The number of turns per inch in the yarn has varied with the individual fabrics, but the range for 150-denier yarns was of the order of 50–60. With open winches it was frequently found that fabrics appeared "nitty" owing to the relatively untwisted yarns in the fabric being well penetrated and uniformly dyed, whereas the highly twisted yarns were not uniformly penetrated, and gave a speckled appearance to the fabric. In order to overcome this defect, it was necessary to dye for a further period, possibly of the order of two hours in the worst cases. It has been found that when using enclosed winches the time required to obtain penetration of highly twisted yarns is significantly reduced. In bulk and in laboratory dyeing this has been most clearly demonstrated with certain direct dyes such as Diphenyl Red 7BL, Chlorantine Fast Blue 3GLL, and Chlorazol Fast Scarlet GS. Cross-sections cut from yarns taken from the dye-bath after various progressive periods of dyeing have clearly shown greater penetration of the dye in the case of enclosed dyeing compared with dyeing in an open vessel (Fig. 11).

(*d*) WORKS DYEING TIME

It has been mentioned earlier that with the enclosed winch it is possible to secure not only a higher average dyeing temperature, but also a more uniform temperature of the dye liquor. In this sense "uniform" implies both that there are smaller temperature variations between back and front of the winch and that there are smaller variations of the average temperature with time.

It would be expected that this would lead to more uniform and more rapid dyeing in the enclosed winch, or alternatively a greater amount of penetration in the same time. Laboratory experiments under controlled conditions have indicated that the difference would be quite considerable, but it is difficult to obtain definite and conclusive proof of this under works conditions. This is not surprising, as the actual dyeing time used depends upon the cumulative effect of several factors, such as type of fabric to be dyed, type of shade, experience of operative, ease of matching, and dye formula employed.

In this particular dyehouse a statistical analysis showed that over the past two years there had been a steady reduction in dyeing times of approximately half-an-hour per dyeing per annum due to a number of causes. Examination of the period since enclosing showed that there was at first just a small increase in time, probably due to the changeover, following which the curve resumed its normal downward trend. It is for this reason that it is not possible at present to assess the effect of enclosure on dyeing times, as there is no positive evidence as to whether there would or would not have been a continued downward trend with open winches. It is evident, therefore, that only by a continued watch on dyeing times over a longer period will it be possible to assess the effect of enclosure on the average time of dyeing in the dyehouse. Opinions of the dyers (and opinions are not evidence) are that dyeing times are less because of enclosure.

(*e*) PRECAUTIONS NECESSARY BECAUSE OF THE HIGHER TEMPERATURES OF DYEING

Dyeing at the higher temperatures obtained in an enclosed as compared with an open winch demands that a number of precautions should be taken, otherwise there may be a danger of damaging fabrics. This applies more to fabrics containing thermoplastic yarns, such as cellulose acetate, than to those made entirely from viscose. Additional care must be taken to prevent fabrics from becoming entwined and rubbing on the winch reel, as creases, cracks, or bruised places are more liable to be formed than is the case in an open winch. There is greater penetration of bruised places when dyeing fabrics of satin or similar construction or fabrics containing fine-filament yarns. In all cases it is an advantage to add a lubricant to the dye liquor in order to minimise the friction between the fabric and the winch reel. Soap or an auxiliary product may be used for this purpose, providing it will withstand the temperature and other conditions of enclosed dyeing.

There is also an increased danger of forming creases and cracks if the bath is not cooled down carefully. The temperature should be reduced appreciably before allowing the liquor to drain from the winch and the fabric to form a pile either in the bottom of the winch or on a scray. Particular care should be taken to avoid running the hot fabric in a dry winch. It is recommended that cold water should be added at a place away from the passage of the fabric, before letting the dye liquor away. The shutters should then be opened, and the dye liquor run away whilst adding further cold

water. The process of "cooling down" and running the liquor away should not be carried out too slowly, particularly if one or more of the dyes present in the mixture is of the rapid dyeing type, otherwise the fabric may become slightly off-shade.

(*f*) WINCH REELS

In winch dyeing the fabric in its rope form is usually circulated by being pulled out of the liquor at the front, over a small jockey pulley, then over the reel, and back into the dye liquor (Fig. 4). The entire movement of the fabric under these conditions is due to the pull imparted to it by the reel, which is driven at a suitable speed. This winch reel does not grip the fabric in any way, but relies on the friction between the reel and the fabric and the weight of the wet fabric itself to prevent slippage.

The open winches employed slatted wooden reels, but these have a much shorter life in the enclosed winch, as they work at higher temperatures with steam trapped in the enclosure, and gradual replacement by stainless steel reels has been found necessary.

Initial designs of stainless steel reels were found unsatisfactory, as the fabric slipped, and resort was made to wrapping the reel with a short length of fabric. This provided a temporary cure.

The frictional resistance between yarns and wood and stainless steel has been measured in the laboratory, and the coefficients of static friction when wet have been found utilising dumb (twistless) yarn. These are shown in Table VI.

TABLE VI

Coefficients of Static Friction between Wet Yarns and Winch Reel Materials

	Viscose	Cellulose Acetate
Wood	0·65	0·57
Stainless steel	0·24	0·21
Viscose	0·80	0·58
Cellulose acetate	0·58	0·60

These figures are not strictly applicable to the conditions obtaining in a winch, owing to the fabric structure and the high temperature, but they give a useful guide. They show that the friction between yarn and stainless steel is very much lower than that between yarn and wood, so that for similar reels in stainless steel and wood, the former would be expected to slip much more than the latter. Apart from wrapping, a permanent cure would have to be sought in a change of design of reel.

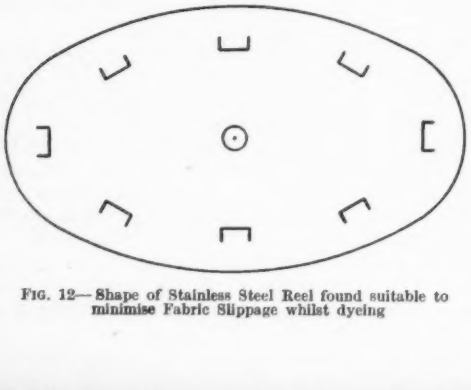


FIG. 12—Shape of Stainless Steel Reel found suitable to minimise Fabric Slippage whilst dyeing

After experiments, the shape shown in the accompanying drawing (Fig. 12) was found suitable for stainless steel.

(5) Other Effects of using Enclosed Winches

(*a*) WORKING CONDITIONS

Steamy atmospheres and wet floors are usually associated with dyehouse working conditions. Most dyehouses make some provision for removing steam by the use of false roofs, exhausting air and steam from the room by means of fans, or by blowing hot air into the room. The dyehouse in question employed a dual system of fan extraction and blowing hot air into the room, but in common with other dyehouses there was often a wall of steam, particularly during the early morning of the winter months. As the number of enclosures was increased it was interesting to note the gradually improving working conditions. On completion of the enclosure of all the winch becks little or no steam could be seen in the dyehouse even during the November months. The floors were dry, excepting where water had been spilled or allowed to overflow. The operative can now reasonably wear shoes, and his collar is no longer like a piece of rag at the end of the day.

(*b*) RETURNS

In all dyeing and finishing works, fabrics are returned from the finishing department and examining department for redyeing owing to the presence of some faults. One common fault is caused by "droppings" from the roof, beams, or shaftings, due to condensation of steam. Some of the "spots" made on the fabric are extremely difficult to remove, particularly those containing creosote from the wood roof beams. Experience has shown that this type of fault has been eliminated by the use of enclosed winches.

(*c*) MAINTENANCE OF BUILDINGS

One of the major problems in dyehouse maintenance is that of the rotting of wood in roof structures. It is undoubtedly true that the main cause of such rotting is the presence of steam in the dyehouse. Repairs to dyehouse roofs are always difficult and expensive to carry out, and usually involve the stopping of machines below the roof section under repair. Moreover, frequently such rotting is not obvious unless the roofs are closely inspected, since most wooden roofs are either slated outside or covered with a waterproof coating of fabric, and it is between the wooden roof and the covering that rotting takes place. The inside may look all right, but between the wood and the covering extensive rotting may have occurred. It is true that rotting can be minimised by keeping the roof warm, and so preventing condensation, but this is expensive. By using enclosed machines the necessity for exhaust fans and Thermoliers in the roof is reduced, as less steam has to be dealt with. It is a fair assumption, therefore, that the life of such a roof will be much lengthened and that, over a number of years, there will be a considerable saving in roof maintenance costs.

(*d*) FUTURE DYEHOUSE DESIGN

A good deal has been written about dyehouse design. One of the main factors that architects have had to consider has been the means of dealing with steam in the dyehouse. False roofs, suitably heated double roofs with a suitable insulation between, have been suggested and indeed used. Trunking has played a part in some. Such means of dealing with steam in the atmosphere certainly give better conditions than an orthodox building, but they are expensive. It is suggested that by the use of enclosed machines future dyehouse design will be simpler, and less expensive, because of the relative absence of steam.

Since we first gave this lecture, a paper has been published in Germany[11] which supports some of our figures.

The authors wish to thank the directors of Messrs. Courtaulds Ltd. for permission to publish this paper.

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WEST RIDING SECTION

Meeting held at the Great Northern Station Hotel, Leeds, on 15th February 1949, Dr. T. A. FORSTER in the chair

The Swelling of Textile Materials

G. KING

INTRODUCTION

One of the most important properties of textiles is their ability to absorb various chemical reagents, either from the vapour phase or from solution, in a more or less reversible manner. Knowledge of this property has become commonplace in the textile world, and, as usual its technical application has rapidly outstripped the necessary scientific interpretation. It is not easy to realise, therefore, how limited is our real understanding of the subject. Furthermore, this defect will not be fully remedied until a more complete theory of liquids becomes available, as these swelling and adsorption processes are in many ways analogous to those involved in the mixing of two liquids.

In this paper it is proposed to give a rough survey of recent investigations carried out by the Wool Industries Research Association into the absorbing properties of keratin and nylon. Because of the complicated nature of the problem, very simple systems have been used in which a single swelling agent is adsorbed from the vapour state in an evacuated system. The implications of the various results obtained will be discussed in the light of present-day conceptions of the swelling process.

The ability of chemical reagents to swell or be adsorbed by polymeric materials follows roughly the laws governing the miscibility of liquids, and one can apply the old maxim that "like dissolves like" with a certain measure of success. Whereas hydrocarbon polymers such as rubber are swollen largely by hydrocarbon solvents, only polar solvents are adsorbed to any great extent by polar polymers, which constitute the greater proportion of textile materials.

The most common of all such polar swelling agents is, of course, water, and it has therefore received most attention from investigators. Much of the work has been directed to investigation of regain curves, no doubt as a result of the importance attached to regain standardisation in the

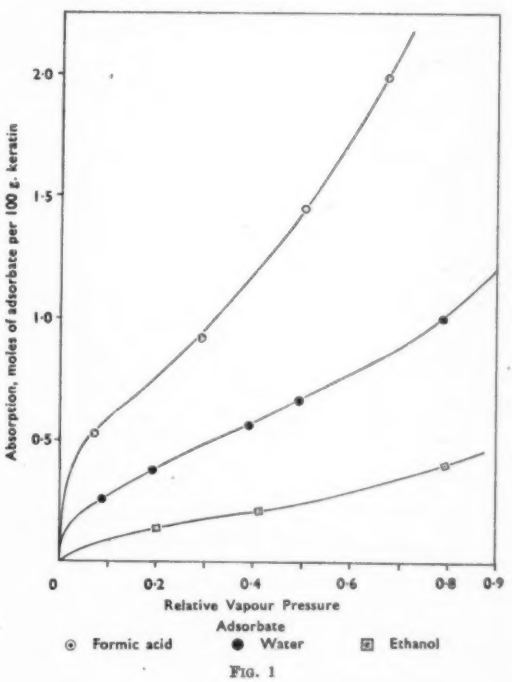

FIG. 1

trade. The regain curve for the wool–water system has been discussed in great detail at a recent symposium of the Society[1], and it is not proposed to deal with it at any great length in this paper. It may be pointed out, however, that in the case of wool, similar regain curves may be obtained with other swelling agents (Fig. 1), and that a similar theory should apply in all cases. In short, the adsorbate may be divided into two fractions, one chemically bound to specific sites, and predominating in the early stages of adsorption, and the other adsorbed by a mixing process at a later stage.

SWELLING RELATIONS

As the adsorption proceeds, the adsorbent naturally increases in volume, the swelling being anisotropic when the polymer is in the form of a fibre, for in this special case the long molecular chains are aligned more or less parallel to the fibre axis. The increase in volume is not directly proportional to the regain of the polymer. Initially the adsorbed molecules occupy a volume less than they did in the liquid state, and it is only in the later stages of adsorption that the increase in volume per unit mass adsorbed approaches the specific volume of the liquid adsorbate. Typical swelling relations for nylon–water[2], keratin–water[3], and cellulose–water[4] systems are shown in Fig. 2.

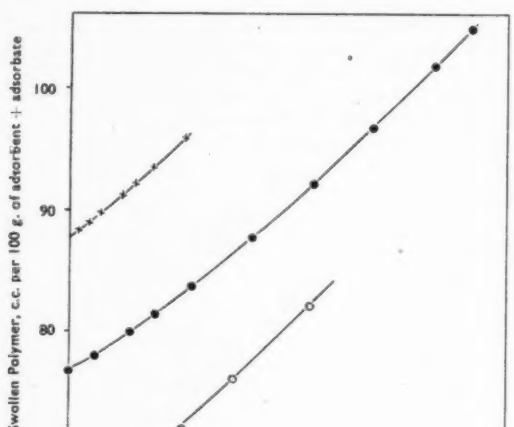

FIG. 2

This restricted initial swelling has been the subject of no little speculation, and it has been suggested that the adsorbate must be subject to enormous pressure within the polymer. In the case of water, for example, in the adsorbed state it may achieve an apparent density of almost double the normal value. But, as mentioned before, these swollen polymer systems have many physical aspects in common with liquids, and in this respect it is enlightening to review the case of the sulphuric acid–water system. As water is added to sulphuric acid, we have again a limited increase in volume for low water concentrations, such that the estimated density of the water in solution may also rise to a maximum of 2 g./c.c.

In this latter case it has never been suggested that such an apparent contraction was due to compression of the water. Instead, it is generally accepted that the water molecules are chemically bound to the sulphuric acid molecules, and can no longer be considered as liquid water. Similarly in the case of the swollen polymer one should not assume that the adsorbate retains its original liquid form, for in the early stages of adsorption in particular it consists of isolated molecules attached to separate adsorption sites. Such molecules form an integral part of the polymer structure and are analogous to water of crystallisation.

It is very probable that the free volume of these bound molecules will be less than that available to them in the liquid state. Few liquids have a perfectly close packed structure, for most molecules depart considerably from spherical symmetry, and internal forces such as hydrogen bonds tend to impose a structure on the system. Typical examples of such liquids are acids, alcohols, and water. In the last case a close packed liquid having molecules of the known size of water molecules would have a density of 2 g./c.c., which is of the same order as the abnormal values found for adsorbed water.

Finally, because of the imperfectly crystalline state of most polymers there may be an appreciable amount of free space available in the polymer itself, such that adsorbed molecules may be accommodated without distorting the lattice to any great extent. It is plain, therefore, that this initial portion of the swelling relation may be accounted for without great difficulty.

The later stages of the swelling relation provide scope for speculation also. In the case of wool keratin, at about 20% regain, the swelling increment per unit weight of adsorbate is very nearly

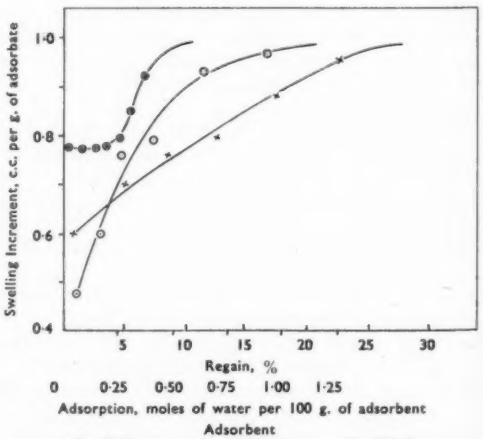

FIG. 3

equal to the specific volume of liquid water, suggesting that liquid water is present in the polymer (Fig. 3). Now the total mass of the adsorbed water molecules constitutes only one-sixth of the total mass of the swollen polymer, and according to present conceptions of the adsorption process, they will be distributed about the adsorbent in a series of clusters, each of which will contain on the average less than two water molecules[5]. But it takes more than two water molecules to constitute liquid water, especially when one of these molecules is firmly bound to the adsorbent.

Of course, we are dealing with a kinetic equilibrium, and at any instant there may be more than two molecules in a particular cluster, but such a probability decreases rapidly with the number per cluster. It is also difficult to see how the polymer lattice could accommodate sufficient water molecules at one point, such that liquid water could be said to be present.

This point has been raised by Gilbert and Rideal in a recent paper on the theory of dyeing[6]. They point out that when wool is adsorbing dye from solution, it is incorrect to assume that the adsorbed dye ions are in a liquid environment. Such an assertion seems very reasonable in view of the foregoing argument, for a dye ion must be enclosed in at least a complete shell of water molecules before its environment approaches that of liquid water.

If we examine the nylon–water and cellulose–water swelling relations in Fig. 3, we find that the volume increment per unit mass adsorbed approaches unity at water concentrations as low as 8% and 14% respectively. In other words swelling does not follow a simple law of mixing of liquid water with the polymer substance.

It is probable that this relation is to be associated with the change in state of the swollen polymer as a whole. Many long-chain compounds undergo what is termed a second-order phase transition as their temperature is raised or lowered[7]. The change has been described as an internal melting, and not only does the polymer change from a brittle to a rubber-like state, but many of its physical constants alter in value. The presence of plasticising agents lowers this transition temperature, and increasing concentration of plasticising agent may even cause such a change at constant temperature.

Now dry nylon undergoes such a transition at about 47°C., when, together with other changes, its dielectric constant increases rapidly[8] and its elastic moduli are reduced[9]. On the other hand, the transition temperatures for dry keratin and cellulose are too high to be measured, but in all three cases these characteristic temperatures can be lowered by the adsorption of water until such changes take place at room temperature. Fig. 4 shows typical examples of the change in the elastic moduli of wool, nylon, and cotton with regain at normal temperature. It will be observed that these relations bear a marked similarity to those in Fig. 3, suggesting that both are manifestations of the same phenomenon.

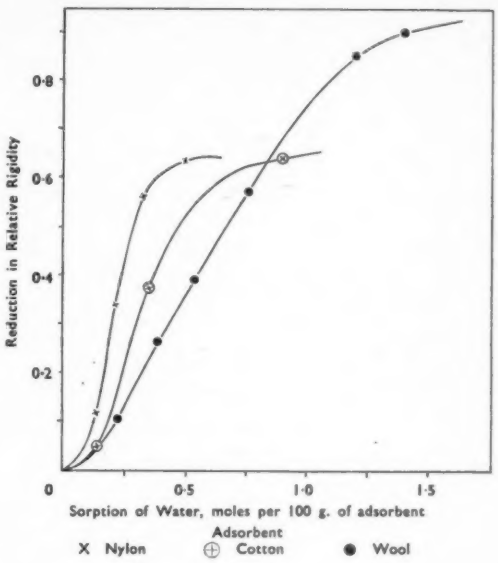

FIG. 4

CRYSTALLINE AND AMORPHOUS FRACTIONS

One would naturally assume that swelling takes place uniformly throughout a given polymeric material, provided the latter is in a reasonably pure state. In recent years, however, there has accumulated a certain amount of evidence that, in the case of water, a certain fraction of some polymers is not available to the adsorbed molecules during the swelling process.

This phenomenon can be demonstrated quite readily in the case of nylon. The chemical formula of the adipamide or "six-six" nylon polymer is known, and thus the concentration of the polar groups can be calculated. These consist chiefly of –NH·CO– groups, of which there is 0·88 mole per 100 g.

It is reasonable to assume that these groups supply the low-energy sites for the bound water molecules. This being so, it becomes a relatively easy matter to make an estimate of the number of these sites, using measurements of the total and partial heats of wetting of nylon by water[9,10]. The partial or differential heat of wetting at zero regain gives one the heat of adsorption per bound molecule, while the total heat of wetting gives the total heat evolved by all the bound water molecules; and in the case of nylon, where there is little swelling, the ratio of these two quantities indicates the number of available sites.

The result suggests that only about 0·2 mole of sites is used, i.e. only one-quarter of the available polar groups. This low value is confirmed by comparison of the regain curves of nylon– and keratin–water systems. In the latter case it has been estimated that there are 1·1 moles of adsorption sites per 100 g., a value which compares favourably with the concentration of polar groups in nylon, but examination of the isotherms in Fig. 5 suggests a much lower value for the nylon–water system.

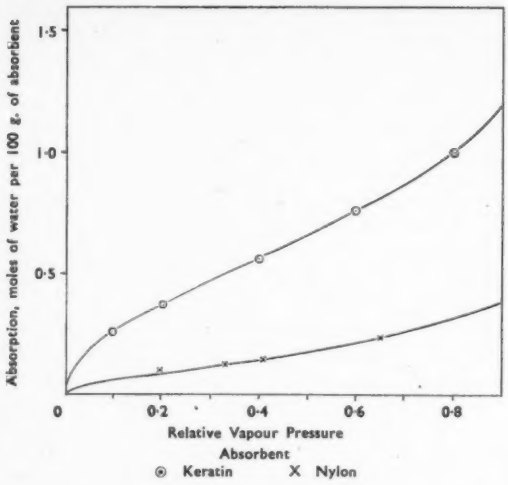

FIG. 5

One possible explanation of this phenomenon is based on modern conceptions of the physical structure of long-chain polar substances. As mentioned earlier, there is reason to believe that these materials are partly crystalline and partly amorphous, with many molecular chains passing through both regions in turn, as shown in Fig. 6.

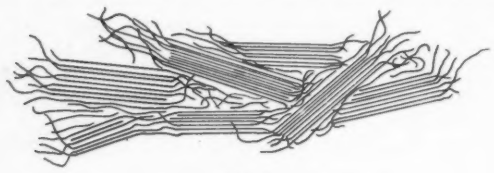

FIG. 6

Now the adsorption of water does not, in general, affect the X-ray interference pattern produced by such a polymer, and as this is contributed by the crystalline fraction alone, it must be concluded that water is adsorbed only by the amorphous fraction.

EQUILIBRIUM CONDITIONS

For the swelling relations just discussed, it has been tacitly assumed that we were dealing with a series of equilibrium conditions. This is not necessarily true, and it is of paramount importance to examine the laws which determine the rate of attainment of these equilibria. For example, the wool–water system in particular exhibits a hysteresis effect for the sorption–desorption cycle. If one repeats such a process using either ethyl alcohol and wool, or water and a fairly thick horn film, one finds the hysteresis to be grossly exaggerated (Fig. 7).

These phenomena are no doubt linked with the conclusions of some investigators that a polymer swells more extensively as a fibre than in bulk[11]. This is probably due to the assumption that sorption and swelling are instantaneous processes. But in the fibre state we are dealing with the polymer in a very finely divided form, in which the total

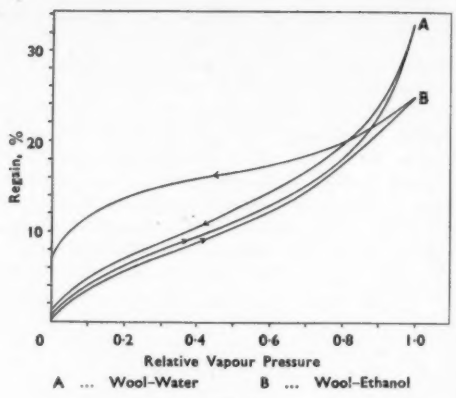

FIG. 7

surface area is very large for a given mass of material and the adsorption is rapid.

This is not the case for a thick film of the same polymer. Consider, for example a finger nail. It is chemically similar to a wool fibre, yet the nail adsorbs water so slowly that it would take days for it to acquire a regain of about 25% from dryness. If, however, we could reduce the nail to a quantity of shavings, we should find that these reproduced the adsorption properties of wool very closely.

On drying out such a thick film of horn, one finds that, at first, water is evolved much more rapidly than it was adsorbed (Fig. 8). The rapid desorption

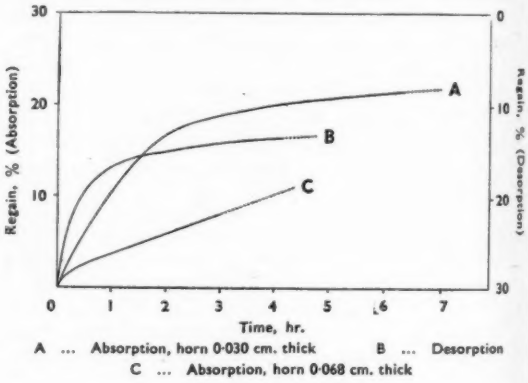

FIG. 8

rate soon falls away, however, and a quasi-equilibrium is attained with about 7% of water remaining in the specimen after extensive drying, and it is not possible to remove this residual water in a reasonable time by further drying at room temperature. The amount of this residual water is found to depend on the film dimensions, becoming less for thin films, and, of course, very small in the case of wool fibres.

However, in the case of wool the residual water is not entirely negligible, as one soon realises when endeavouring to determine the exact dry weight of a sample. Accurate investigations have shown that a perfectly dry state is never obtained,

the actual value depending on the drying technique[12].

Now if we increase the size of the absorbate molecule, the residual concentration becomes very important, even when wool is the adsorbent. It is well known, for example, that after wool has been swollen with methyl alcohol, it is not possible to remove the last 6% of alcohol except by washing in water. These results led to the natural conclusion that the residual alcohol was intimately bound to the polymer. But this would suggest that alcohols were more firmly bound in the adsorbed state than water, which is in contradiction with the fact that they may be replaced by water.

This and other anomalies have been explained, however, as a result of investigations into the rate of diffusion of vapours through textile polymers[13,14]. It may be demonstrated that if a water concentration gradient is produced across a horn membrane, such that one side remains dry while the regain of the other is gradually increased to saturation, then the flow of water vapour through the membrane increases, not linearly with the difference in concentration, but exponentially. In effect water diffuses through keratin extremely slowly at low regains (Fig. 9).

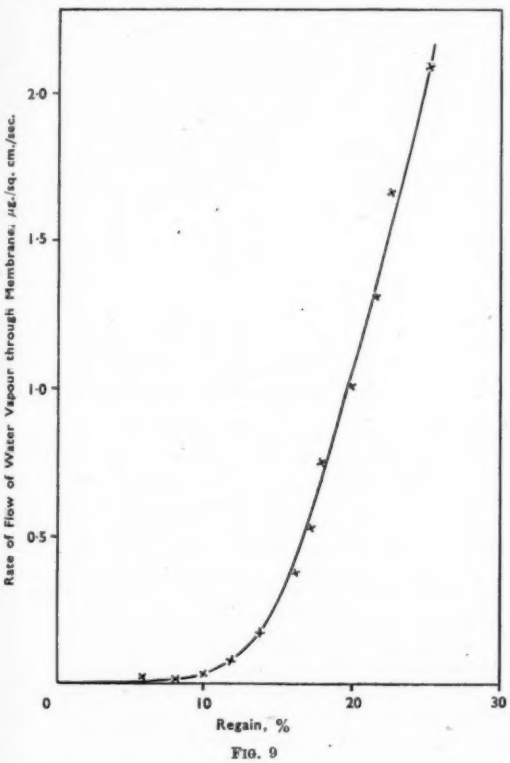

FIG. 9

When drying out a swollen polymer, the outermost layer becomes dehydrated first, so that the adsorbate remaining in the centre of the specimen can only be removed very slowly through this barrier. In effect a fraction of the adsorbate is trapped within the polymer.

Because of this slow diffusion of water through dry keratin it is evident that even in the case of a wool–water system it is dangerous to assume that absolute equilibrium conditions can be established at low regains at room temperature. Similar doubts exist even in the case of formic acid, which at normal concentrations is adsorbed by wool about twenty times as fast as water, for at low regains the rate of adsorption falls to nearly one-tenth of that for water at comparable regains.

If these conditions exist in the case of water and formic acid, how much more important must this factor become as we proceed to higher members of the corresponding homologous series, for it has been found that the rates of adsorption of the aliphatic alcohols by wool decrease exponentially with increased molecular weight of the adsorbate[15] (Fig. 10). In particular, whereas wool adsorbs

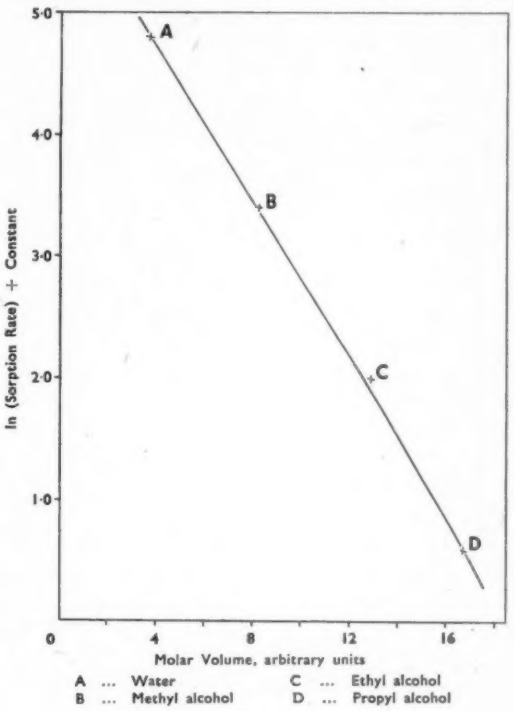

FIG. 10

about 16% of water in one hour in an evacuated system, it takes several days to adsorb an equal proportion of propyl alcohol.

An interesting example of the danger of presuming a state of equilibrium under these conditions is given by recent work on the maximum swelling of keratin and other fibres in homologous series of solvents[16]. The results appeared to indicate that the adsorption of the higher homologues was greatly restricted at normal temperatures, and this fact was quoted as being in agreement with the pore theory of adsorption[17]. Such pores would, of course, act as a molecular sieve and exclude all molecules over a certain size.

It seems very unlikely that we are dealing with a true equilibrium in the case of these large molecules, and this is supported by the further evidence that an increase in temperature was found to increase the sorption of these higher members. For a true equilibrium, such an increase in temperature would in all probability lead to a decrease in sorption, as the sorption process is exothermic at these low molar concentrations.

On the other hand, a temperature increase would greatly increase the rate of adsorption, as it certainly does in the case of propyl alcohol and wool, and this should displace the quasi-equilibrium to a higher value.

SWELLING POWER OF SOLVENTS

There have been many attempts to measure the swelling power of adsorbates for different polymers. Some investigators measure this in terms of the volume at maximum swelling[16]; others have determined the effect of the swelling agent on some property of the polymer[18]. At Torridon we have made some use of the second method. Modulus of rigidity–sorption relations have been determined for keratin and nylon using water, methyl alcohol, and formic acid as adsorbates[9,19]. As shown in Fig. 11, the reduction in rigidity per mole adsorbed

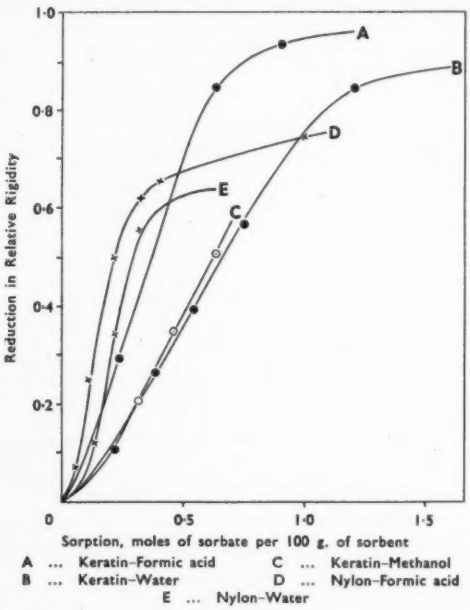

FIG. 11

is about the same for water and the alcohol, but much more rapid in the case of the acid.

This exceptional swelling power of aliphatic acids is, of course, a well known phenomenon, and is attributed, rather vaguely, to their acidic nature. But it is difficult to visualise them as ionised to any great extent when adsorbed, i.e. surrounded by a medium of low dielectric constant. Some light has been thrown on this problem as the result of recent work on the electrical properties of textile materials[20]. In their swollen state these polymers have a relatively high dielectric constant and D.C. conductivity compared with the values obtaining in the unswollen state.

Now it becomes increasingly evident that D.C. conduction takes place through these systems by a form of ionic migration analogous to that in normal solution, for electrolytes are generally present as impurities in many polymers. The current will therefore be determined by the degree of dissociation of the electrolyte and the viscous restraint imposed on ionic movement by the molecular structure of the polymer. Of these, the more important factor is the degree of dissociation of the ion pairs, which is in turn determined by the dielectric constant of the swollen polymer. Furthermore, as shown in Fig. 12, a wide range of

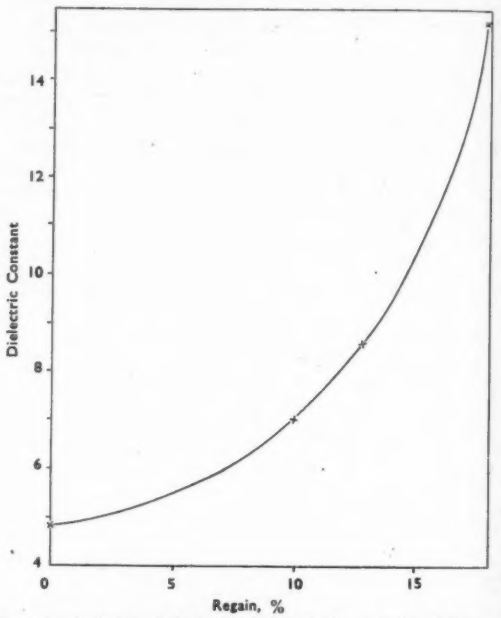

FIG. 12—Variation of Dielectric Constant with Regain of Keratin

dielectric constant values is available for a relatively small range of adsorbate concentrations; thus in the case of the keratin–water system it is possible to pass from conditions of almost complete association at zero regain to almost complete dissociation at about 25% regain (Fig. 13). Thus it is possible to explain the enormous conductivity range of about 10^6 times in these systems, and why free ions can exist in such large concentrations in these swollen polymers in the absence of liquid water.

Now the dissociation constant of water is extremely small, so that even at high regains one would not expect any appreciable dissociation of the adsorbed water. However, this is not the case for formic acid, which has a dissociation constant of 10^3 in aqueous solution, so that in the case of polymers swollen with formic acid, the latter not only produces an increase in dielectric constant by swelling, but becomes as a result increasingly ionised itself at high concentrations, and contributes to the D.C. current (Fig. 14).

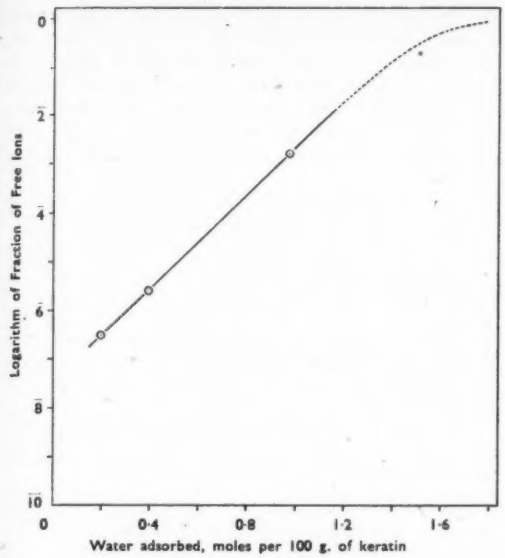

FIG. 13

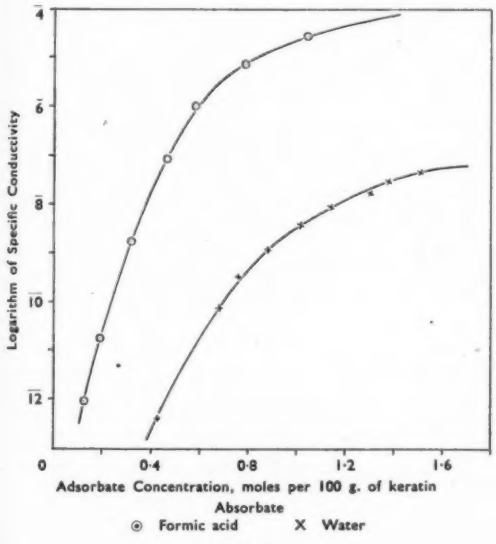

FIG. 14

We have, then, a rough picture of the swelling action of this acid. At low concentration it is adsorbed by reason of its polar nature in a relatively unionised state. Its rates of adsorption and desorption are very low, roughly the same as those for methyl alcohol. Then, as the concentration of adsorbate increases, the acid properties become apparent, there are extensive ionisation and consequent swelling, a rapid reduction in the elastic properties of the adsorbent, and the adsorption–desorption rates exceed even those for water.

The author's thanks are due to the Council of the Wool Industries Research Association for permission to publish this account.

WOOL INDUSTRIES RESEARCH ASSOCIATION
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Discussion

Mr. J. A. C. WATT: Which is the most accurate method of obtaining the dry weight of a sample of wool?

Mr. KING: The standard method of heating the sample to 105°C. in a stream of air previously dried with phosphorus pentoxide gives the most consistent results.

Mr. WATT: How do the results obtained by this method compare with those determined by drying the wool over phosphorus pentoxide in a vacuum?

Mr. KING: The former method will give values about 0·3% lower. The final stages of drying are much slower at lower temperatures, and the dry weight then depends to a large extent on the period of drying.

Mr. H. E. NÜRSTEN: Will the slow diffusion of water through keratin at low regains have any effect on regain determinations in the case of wool? These measurements take a relatively short time, and therefore moisture inside the wool will not have time to diffuse through the dry outer layer.

Mr. KING: This effect is more important when dealing with large masses of keratin, with water as absorbate. In the case of wool fibres we have keratin in a very finely divided state with a large surface area per unit mass, and the absorption process takes place rapidly at normal regains. However, at low regains, i.e. less than about 4%, the diffusion rate is reduced, and the effect becomes important even for wool fibres.

Mr. R. B. WHITEHEAD: Is the prevention of shrinkage in a woollen fabric by the application of a hydrophobic melamine resin due to a reduction in the swelling propensities of the wool fibre?

Mr. KING: In so far as swelling assists the felting of wool, any method which inhibits the swelling should reduce fabric shrinkage.

Mr. G. LANDELLS: There is no doubt that fibre swelling is one of the fundamental causes of dimensional change in cellulose fabrics, and that certain resin treatments produce various degrees of stability depending on their effectiveness in reducing swelling. Fibre swelling is instrumental in bringing about crimp changes in the yarns, and these appear to be the main factor in determining the amount of shrinkage. A number of other factors also play a part; the rigidity of the treated yarns is one which may be important in connection with resin treatment, and any factor which is likely to prevent crimp changes is of interest for stabilisation purposes.

Mr. W. R. MOORE: Studies of the action of organic liquids on synthetic fibres and fibrous cellulose are being carried out in the Chemistry and Dyeing Department at Bradford Technical College. Many of the considerations put forward by the Lecturer for wool hold also for cellulose derivatives, and it is possible, because of their less polar character, to interpret swelling in terms of general theories of polymer–liquid interaction. In particular, similar results have been obtained for the sorption of solvents from solvent–hexane mixtures by cellulose nitrate. An account of this will be published shortly in the *Journal of Polymer Science*.

Dr. C. S. WHEWELL: Can the Lecturer give any information of the swelling of fibres in alcohols at different temperatures? Is the swelling greatly affected by a rise of temperature, and is the diffusion of alcohol vapour or liquid alcohol much faster at high temperatures than at low temperatures?

Mr. KING: The rate of diffusion of alcohol vapour through keratin increases rapidly with temperature at low concentrations in the case of the lower members of the homologous series, and at all concentrations in the case of the higher members, although in this latter case the molar concentration will naturally be low, and the same conditions apply in reality. The slow rate of absorption of the higher members plays a large part in determining the swelling maximum, and this will increase with temperature owing to the increased rate of adsorption.

Mr. J. A. MEDLEY: Is it possible to estimate by X-ray measurements the ratio of the crystalline to the amorphous fraction in nylon, and can this be shown to correspond to the fraction of polar groups which appear to be available as adsorption sites?

Mr. KING: This has been attempted in the case of rubber in order to determine the increase in crystallinity imparted by stretching, and there is no reason why a similar estimate might not be attempted in the case of nylon.

Dr. A. B. D. CASSIE: Will the increased dissociation of formic acid in keratin at high concentrations affect the pH of the system?

Mr. KING: As the acid concentration in the keratin is increased, the hydrogen ion concentration also will increase, and approach that of the water extract. At low acid concentrations in the keratin the hydrogen ion concentration will be less than that in the water extract, owing to the limited dissociation in the keratin.

With reference to the marked hysteresis shown by the wool–ethanol system, at low regains the adsorption cycle will lie below the true value because of the slow rate of adsorption. In the case of the desorption cycle, values are abnormally high because the outer surface of the wool first loses the greater part of its alcohol content, and this restricts any further evolution of alcohol. The results will depend to a large extent on whether the changes in regain are made by gradually changing the vapour pressure or by some discontinuous method.

LEEDS JUNIOR BRANCH

Meetings held at the University of Leeds, on 1st March 1949, Professor W. BRADLEY in the chair, and, in part, on 3rd March 1942, (the late) Professor F. M. ROWE in the chair

Recent Trends in the Search for New Azo Dyes
I—Dyes for Wool

A. H. KNIGHT

Introduction

It is ninety years since Peter Griess discovered the "diazo" compounds and seventy-four years since his "coupling" reaction was applied industrially to the manufacture of Chrysoidine, the orange dye for wool obtained by the action of benzene diazonium chloride on *m*-phenylenediamine. Despite the fact that in the meantime many thousands of azo combinations have been made experimentally and around two thousand differently constituted azo dyes have been or are being manufactured commercially, the search continues for new azo products of enhanced properties of hue or fastness, susceptible to new methods of application, or satisfying entirely new requirements. In addition to their application to the colouring of the older textile materials and their use in making paints and lacquers, azo products are now used for colouring the various rayons and synthetic fibres such as nylon, as well as wood, paper, straw, varnishes, rubber and other plastics, and foodstuffs. They have also found application in medicine.

The recent war will have undoubtedly interfered with both research and patenting on azo dyes by the dye-making firms of the belligerent countries. From a consideration of patents only, it is difficult therefore, to assess the relative distribution of recent effort in these countries over the main topics of azo dye research. However, from an examination of the references given in *Reports on the Progress of*

Applied Chemistry to British patents granted to the three Swiss firms, Ciba, Geigy, and Sandoz, between October 1939 and April 1946, the following approximate distribution is arrived at—

Acid wool dyes	12
Chrome wool dyes	20
Leather dyes	3
Direct cotton dyes	47
Acetate rayon dyes	13
Azoic bases and coupling components	7

These figures suggest that in neutral Switzerland the greatest attention to research on azo dyes immediately before and during World War II was on dyes for cotton, dyes for wool coming second.

Broadly speaking, the main objectives in azo dye and pigment research, apart from meeting the requirements of new fibres and filling gaps in hue ranges, are still increase in light fastness and, in the case of dyes for textiles, in fastness to wet treatments. In many cases, improvements in these directions are achieved by greater chemical complexity of the new dyes as compared with the old, and this often involves increased cost for the desired effect. This question of cost is becoming an increasingly important factor in azo research, as the dye user cannot afford to pay more for the improved properties than his customers are prepared to pay for the given type of business. This is particularly the case if the new azo product approaches in cost other types of dyes already on the market whilst still failing to reach their standard of fastness, as might occur, for example, with direct cotton dyes versus vat dyes.

In such a vast field as that of azo dyes, where the broad chemical relationships to properties and scope of application are well known and the products in many cases are still relatively cheap by comparison with other classes of dyes, improvements in fastness properties or extensions of hue range are usually achieved by a number of small steps rather than by spectacular jumps. Nevertheless, in the last 10–20 years several advances of the latter type have been made.

The research chemist seeking new dyes must keep a watchful eye on developments in other branches of chemical activity and industry, particularly for new reactions or new products which may serve as starting points for new dyes. Thus some of the higher alkylated and aralkylated phenols which have found application in the manufacture of dye auxiliary products or as rubber chemicals in recent years have also appeared in patent specifications as coupling components for new azo dyes.

The present paper is restricted to dyes for wool, while it is hoped that subsequent papers will deal with recent work on azo dyes for acetate rayon, nylon, and cotton, including azoic dyes. In considering these "trends", the word "recent" will be interpreted liberally, and inventions made as many as 15–20 years ago as well as others of more recent date will be considered. Inventions will not necessarily be referred to in chronological order.

Azo dyes for wool fall into two well known water-soluble classes, viz. *acid wool dyes* and *mordant wool dyes*. The former are applied from acid or neutral dyebaths and rely on their initial constitution for the hue and fastness properties they possess. The latter are applied by one or other of four general methods, all of which involve metal-complex formation, usually with chromium. In the process of such metallisation the hue of the parent dye is altered and the fastness properties are improved. In order to respond to metallisation the constitution of the parent must accord with one or other of several well defined patterns.

Acid Wool Dyes

Technical acid wool dyes fall into two main classes, viz. *level dyeing* and *fast to milling*. However, there are a considerable number of commercial dyes which do not fall strictly into either class and have been described as "general purpose" dyes. The level-dyeing dyes have relatively low affinity for wool, and poor or moderate wet fastness, but some have very good light fastness. They are almost invariably applied from a sulphuric acid–Glauber's salt dyebath and usually give bright shades. Examples are—

LISSAMINE FAST YELLOW 2G (*C.I.* 639)
Sulphanilic acid→1-(2′:5′-Dichloro-4′-sulphophenyl)-3-methyl-5-pyrazolone

AZO GERANINE 2G (*C.I.* 31)
Aniline→Acetyl-H-acid

LISSAMINE FAST RED B
4-Aminoacetanilide-3-sulphonic acid $\xrightarrow{\text{Acid}}$ γ-Acid

Dyes which are intermediate between the level-dyeing and fast-to-milling classes include certain monoazo dyes of the type—

Amine→Naphtholsulphonic acid

and certain disazo dyes of the type—

$$A^1 \xrightarrow{\text{Acid}} Z \xleftarrow{\text{Alkali}} A^2$$

These dyes usually level reasonably well from an acid bath, have moderate washing and milling fastness, aré relatively inexpensive, and include dyes of bright hues as well as browns, blacks, and dark greens. Examples are—

NAPHTHALENE SCARLET 4R (*C.I.* 185)
Naphthionic acid→G-Acid

NAPHTHALENE BLACK 12B (*C.I.* 246)
p-Nitroaniline $\xrightarrow{\text{Acid}}$ H-Acid $\xleftarrow{\text{Alkali}}$ Aniline

The fast-to-milling dyes are usually of the chemical classes—

(*a*) E^1←Diamine→E^2

(where E^1 and E^2 are the same or different coupling components) and

(*b*) A→M→E

The hues of the established commercial dyes of class (*a*) range from yellow to red and brown. They vary considerably in light fastness and frequently, although having good milling fastness, they have only moderate fastness to severe (or repeated) washing. They have high intrinsic affinity for the wool fibre and consequently do not level well as judged by the "boiling-off" test, though level dyeings can be obtained by slowing down the dyeing process sufficiently. They are, therefore, usually applied from an acetic acid–Glauber's salt dyebath. Examples of the diaminedisazo type (*a*) are—

SUPRANOL ORANGE 2R (IG)[1]
Acetoacetanilide←*m*-Tolidine→2-Naphthol-6:8-disulphonic acid (G-acid)

COOMASSIE RED R
β-Naphthol←*m*-Tolidine→1-Naphthol-3:6-disulphonic acid

MILLING RED R[2]
R-Acid←4:4′-Diaminodiphenylmethane→R-Acid

The secondary disazo class (*b*) provides reds which supplement those of the diaminedisazo class and in addition provides valuable blue, navy, and black dyes. Examples of established secondary disazo dyes which have good fastness to milling and repeated washing are—

COOMASSIE RED G (*C.I.* 249)
Aminoazobenzene→Neville and Winther's Acid

COOMASSIE NAVY BLUE 2RN (*C.I.* 289)
Metanilic Acid→*α*-Naphthylamine→Phenyl-peri acid

COOMASSIE FAST BLACK B (*C.I.* 307)
1-Naphthylamine-5-sulphonic acid→*α*-Naphthylamine→Phenyl-peri acid

The relationships between coupling components and hue which have formed the main foundations upon which the well-established acid wool dyes have been built are—

(1) Certain pyrazolones or other compounds containing reactive methylene groups and phenols for yellows

(2) Certain naphthols or naphtholsulphonic acids for oranges, reds, and scarlets

(3) Certain acylaminonaphtholsulphonic acids and acid-coupled *γ*-acid for oranges and reds

(4) Alkaline-coupled *γ*-acid derivatives for browns

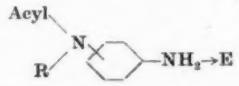
(5) Twice-coupled 1:8-aminonaphtholsulphonic acids and monoazo and secondary disazo dyes from *N*-aryl-peri acids for blues and blacks.

Wet fastness and levelling properties have been dependent on degree of molecular complexity, e.g. simple monoazo compounds for the levelling dyes and disazo for the milling dyes.

Recent developments in acid wool dyes have been mainly directed to producing, on the one hand, levelling dyes of good light fastness applicable from sulphuric acid–Glauber's salt dyebaths but with better fastness to wet treatments and, on the other hand, milling dyes with a high order of washing fastness combined with good light fastness for application from weakly acid or neutral dyebaths. Hitherto, it has been pretty well accepted as axiomatic that a well levelling acid dye cannot be fast to wet treatments and, conversely, that a dye fast to washing and milling cannot be level-dyeing; the two sets of properties have appeared to be mutually exclusive. A certain amount of effort has also been directed to producing dyes having better levelling properties than the traditional level-dyeing types already exemplified, but with no material improvement in fastness to wet treatments. A preference for attempting to secure these effects from monoazo structures can be discerned, probably on account of the greater ease in manipulating the variations in constitution necessary and the generally greater brightness of shade and degree of light fastness given by such combinations as compared with polyazo dyes containing the same types of components.

MONOAZO ACID WOOL DYES

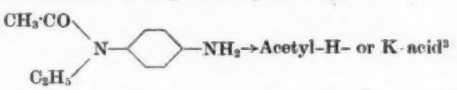
(*a*) SOME RELATIONSHIPS BETWEEN CONSTITUTION AND PROPERTIES— It may be of interest to illustrate in some detail the possibility of building up, from a general formula containing several variables, monoazo acid wool dyes of varying shade and levelling properties and widely varying fastness to wet treatments. Patents have been taken out by numerous dyemakers for dyes of the general formula—



where R has been alkyl (short- and long-chain, straight- and branched-chain), *cyclo*alkyl, aralkyl, aryl, sulphoalkyl, or carboxymethyl; and E has been, variously, a sulphoarylpyrazolone, naphtholsulphonic acid, acid-coupled *γ*-acid, or one of certain acylaminonaphtholsulphonic acids and *N*-aryl-*γ*-acids. The acyl group on the diazo component has ranged variously in different patents, e.g. from acetyl to butyryl, formyl and alkoxyformyl, alkoxyacetyl and aryloxyacetyl (with substituents such as halogen or methyl in the aryl group), *cyclo*hexyloxyacetyl, benzoyl and substituted benzoyl, and arylsulphonyl. The acylaminonaphtholsulphonic acid coupling components include derivatives of the well known H-, K-, J-, M-, and *γ*-acids as well as those of the lesser known 1-amino-8-naphthol-6-sulphonic acid.

Let us attempt to sort out some of the effects claimed for the use of particular groupings in the dyes covered by these patents.

The constitutionally simplest members of this series can be exemplified by the dyes—



which are levelling dyes, similar in this respect to Azo Geranine 2G (*C.I.* 31), yielding bluish-red dyeings and said to have particularly good fastness to sea-water. Replacement of the ethyl group in the diazo component by a branched-chain alkyl group such as *iso*propyl or *iso*- or *sec*.-butyl[4] is said to yield clearer and yellower hues and, in so far as the acyl groups remain the same, the levelling properties are similar. Replacement of the acetyl group by benzoyl or *p*-toluenesulphonyl confers some additional wet fastness.

If a *cyclo*hexyl group is used in place of ethyl in the diazo component the resulting dyes are said to be distinguished from those having the latter group not only by a clearer, yellower hue, but also by an increased affinity for wool and a better fastness to washing and milling. It is said that in many cases the light fastness is also better[5]. The increased fastness to wet treatments is reflected in levelling properties inferior to those of corresponding dyes containing a short-chain alkyl (e.g. *iso*propyl) group[4].

If a long-chain alkyl group (e.g. decyl or cetyl) replaces ethyl in the above formula then dyes of very high fastness to washing and milling are obtained (see later under "Monoazo Milling Dyes").

Replacement of the ethyl by a sulphoalkyl group (e.g. β-sulphoethyl) yields dyes distinguished from the analogous ethyl derivatives by greater water-solubility, better levelling power, and, in certain cases, a better fastness to sea-water. Moreover, the presence of the sulphoalkyl group makes it possible, while using non-sulphonated coupling components, to obtain water-soluble products[6]. Diazo components having the carboxymethyl group in place of ethyl have also been the subject of a patent specification relating to brown dyes for wool from *N*-aryl-γ-acids as coupling components[7].

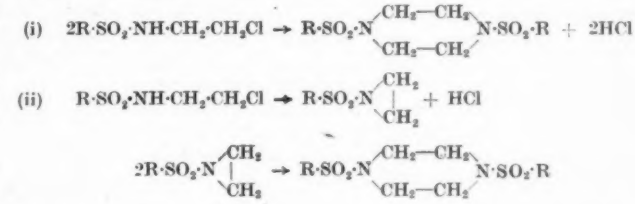
Acyl groups in the diazo component play their part in affecting the hue, fastness, and levelling properties of the derived dyes. Their effect is similar when the coupling component is an acylaminonaphtholsulphonic acid. Some, like the acetyl, benzoyl, and benzene- and *p*-toluene-sulphonyl groups, have been used in wool dyes for many years. More recently others such as the alkoxyacetyl (e.g. methoxyacetyl)[8], aryloxyacetyl (e.g. phenoxy- or chlorophenoxyacetyl)[9], *cyclo*-hexyloxyacetyl[10], and dialkylaminoacetyl[11] groups have been used in making acid wool dyes, and even such complicated acyl groups as

$$-CO\cdot Alkylene\cdot NR^1\cdot SO_2\cdot R^2$$

(R^1 = H, alkyl, aralkyl, or aryl; R^2 = alkyl, aralkyl, or aryl)[12]. Definite advantages are claimed for them in the relevant patents. For example, the dyes containing the aryloxy-acetyl or -propionyl groups are said to be distinguished in general by their fastness to light and milling as well as by their capacity for even dyeing, and to be suitable for discharge printing on wool. Those containing an alkoxyacyl group (e.g. methoxy-acetyl or butoxyacetyl) are said to give yellower hues than corresponding dyes having no alkoxy group attached to the fatty acid group. The use of *N*-acyl derivatives of 1-amino-8-naphthol-6-sulphonic acid as coupling components for monoazo dyes is said to result in better fastness and levelling properties than when the corresponding acyl derivatives of 1-amino-8-naphthol-disulphonic acids are used (e.g. H- and K-acids)[13].

(*b*) Dyes applicable to Wool from a Sulphuric Acid Dyebath (as for Levelling Dyes) and having Good Wet Fastness Properties— Attempts to secure a high degree of washing fastness by use of specially constructed dyes capable of being applied to wool by the method used for the level-dyeing acid dyes (e.g. 3% sulphuric acid and 10% Glauber's salt on the weight of material to be dyed) have been made by both the I.G. Farbenindustrie A.-G. and I.C.I. Two main methods have been employed, both involving the use of chlorine- or bromine-containing compounds. The first, used by both firms in their patents, has consisted in modifying the structures of simple level-dyeing types by employing an ω-chloroacetyl-amino group as substituent. I.G. have made such groupings substituents of naphtholsulphonic acid coupling components[14] and I.C.I. have also introduced them into diazo components[15]. Thus, if Azo Geranine 2G (aniline→acetyl-H-acid) is modified by using ω-chloroacetyl-H-acid as the coupling component instead of acetyl-H-acid, a considerable improvement in fastness to washing, milling, and perspiration occurs. A similar marked effect is produced if, instead of using aniline as the diazo component in Azo Geranine 2G, there is used *m*-amino-ω-chloroacetanilide, 4-amino-1-*N*-ethyl-ω-chloroacetanilide, or 4-amino-2-*N*-ethyl-ω-chloroacetotoluidide. Lissamine Fast Yellow 2G (*C.I.* 639) is sulphanilic acid→1-(2′:5′-dichloro-4′-sulphophenyl)-3-methyl-5-pyrazolone. Yellows of much superior fastness to wet treatments are obtained by using 3-amino-ω-chloroacetanilide-4-sulphonic acid or the above chloroacetylated diazo components instead of sulphanilic acid[16]. The high order of wet fastness produced, which is reflected in the small extent to which the dyes boil off on to white wool, suggests that some chemical combination of dye with wool may have occurred, possibly between the reactive halogen of the halogenoacyl group and amino or mercapto groups in the wool.

The second method, investigated by I.G. and described by an American team of investigators[17] as well as in two French patent specifications[18], consists in employing dyes containing an $-SO_2\cdot NH\cdot CH_2\cdot CH_2Cl$ group. Such dyes possess, initially, level-dyeing properties from a sulphuric acid dyebath. It is said by I.G. that on subjecting them, particularly at 85°c., to a washing which involves an alkaline treatment the dyeings exhibit a quite high degree of fastness. I.G. believed this good wet fastness to be due either (i) to the combination of two molecules of dye with elimination of hydrogen chloride and formation of a piperazide ring directly under the influence of the alkali present in the washing treatment, or (ii) to formation on the fibre of an ethyleneimide followed by dimerisation—



These views were supported by the facts that replacement of the second hydrogen atom of the sulphonamide group by, say, methyl resulted in complete loss of the washing fastness effect, as did the use of the *N*-β-hydroxyethylsulphonamide in place of the chloro derivative. Increase in the length of the alkyl chain in the *N*-ω-chloroalkyl-sulphonamide group also was said to diminish the washing fastness effect[17].

(*c*) Monoazo Milling Dyes— It has already been indicated that the well established milling dyes are *disazo* in type, and therefore of fairly high molecular weight. They possess a higher affinity for wool than simple monoazo acid dyes, and are usually applied from weakly acid dyebaths (e.g. with acetic acid and Glauber's salt). In recent years patents have appeared for *monoazo* dyes capable of

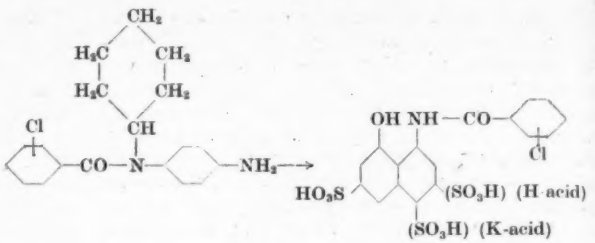
application by similar methods and therefore, by inference, having a good natural affinity for the fibre. Such dyes are said to have good fastness to washing and milling and, in many cases, to light also. These results have usually been secured by weighting the molecules of simple acid dyes.

Deutsche Hydrierwerke A.-G. described in 1931 the preparation of dyes of various kinds (azo, anthraquinone, triphenylmethane) having soap-like properties[19]. These dyes contained hydroxyl or amino groups esterified or acylated by means of a long-chain fatty acid of the soap-forming type. It was claimed that textile materials could be simultaneously dyed and rendered water-resistant with them. Thus H-acid was made to react with stearoyl chloride to give *N*-stearoyl-H-acid for use as a coupling component. I.G. followed this by introducing the long alkyl chain as part of an acyl group in acylphenylenediamine diazo components and acylaminonaphtholsulphonic acid coupling components specifically for wool dyes, which were stated to have very good fastness to washing and fulling[20]. I.C.I. then employed long-chain alkyl groups, e.g. decyl–octadecyl C_{10}–C_{18}, by attaching them to diazo components either directly, as in *p*-cetylaniline[21], as parts of ester[22] or sulphonamido[23] groupings, or as the alkyl in *p*-amino-*N*-alkylacylanilides[24] and aminobenzoyl-*N*-alkylanilines[25]. These dyes have very high neutral affinity and excellent fastness to severe washing and milling. A range giving hues from yellow to red and brown can be built up by choice of suitable coupling components, and violet and blue dyeings with similar wet fastness properties have been obtained from sulphonated anthraquinone derivatives suitably substituted by similar long-chain alkyl groups[26].

J. R. Geigy A.-G. have similarly used *o*- and *p*-aminophenyl alkyl (octyl–octadecyl) ethers as diazo components[27], and Sandoz A.-G. have acylated a sulphonamide grouping in a diazo component with a long-chain fatty acid in preparing yellow pyrazolone dyes, which are said to have high fastness to light and wet treatments; e.g. metanilic octadecanoylamide→dichlorosulphophenylmethylpyrazolone[28].

Azo dyes for wool containing long alkyl chains, as well as some of the anthraquinone series, have been included in the Carbolan range of dyes marketed by I.C.I. They are best applied to wool from a neutral dyebath containing ammonium acetate. The dyebath becomes slightly acid towards the end of the dyeing operation owing to the acetic acid liberated, which promotes exhaustion. It is also of interest to note that compounds containing long-chain aliphatic groupings have been used as colour-couplers in colour photography to prevent diffusion of the couplers through the gelatin of the emulsion.

I.C.I. have also produced monoazo red dyes fast to washing, milling, and light by combining diazotised *N*-chloro- or *N*-bromo-benzoyl-*N*-*cyclo*hexyl-*p*-phenylenediamines with *N*-chloro- or *N*-bromo-benzoyl-H- and K-acids[29], e.g.—

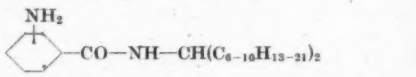


Here again, the increase in molecular weight effected by introducing the *cyclo*hexyl and halogenobenzoyl groups has transformed dyes having poor washing and no milling fastness, e.g. the parent—

$$\text{Aniline} \xrightarrow{\text{Alkali}} \text{H- or K-Acid}$$

$$\text{or Aniline} \longrightarrow \text{Benzoyl-H- or K-acid}$$

into dyes having good properties in these respects. Sandoz, working along similar lines, have patented fast yellow dyes from diazotised *N*-benzyl-*N*-benzoyl- or -benzenesulphonyl-*p*-phenylene-diamines and sulphoarylpyrazolone coupling components. These are said to be particularly suitable for application to wool or silk from neutral dyebaths[30]. I.G. have used as diazo components aminobenzoyl derivatives of mixtures of amines obtained by reaction of carboxylic acids (from oxidation of mixtures of paraffins) with ammonia and hydrogen under pressure[31], e.g.—



Monoazo dyes from 4-amino-2′:3′:4′:5′-tetrahydrodiphenyl and *p*-*cyclo*hexylaniline are referred to in the following section.

DISAZO MILLING DYES

Recent work on disazo acid dyes has also made use of some of the devices mentioned under monoazo dyes. Thus, bromo- and chloro-acetylated diazo components have been used by I.C.I.[32] in building up blues and blacks of the type—

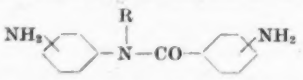
$$A^1 \xrightarrow{\text{Acid}} \text{H-, K-, or S-Acid} \xleftarrow{\text{Alkali}} A^2$$

the halogenoacylamino group being in either A^1 or A^2.

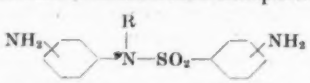
The use of "weighting" groups in disazo dyes of similar type is seen in I.G. patents wherein the alkaline-coupled diazo component is a 4-amino-1-*N*-*cyclo*hexylanilide of a long-chain fatty acid, e.g.—

o-Chloroaniline $\xrightarrow{\text{Acid}}$ H-Acid $\xleftarrow{\text{Alkali}}$ 4-Amino-1-*N*-*cyclo*hexyldecanoanilide[33]

Dyes derived from diaminobenzanilides—



in which R is a long-chain alkyl group[34] or a benzyl group[35], and from diaminobenzenesulphonanilides—



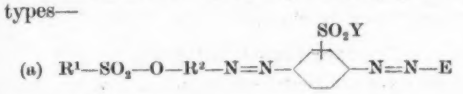
in which R = alkyl (C_1–C_4) or aralkyl[36], have been patented by I.C.I.; the hues range from yellow

to red and brown depending on the coupling components used.

The type of constitution used by Geigy in some of their Polar dyes, wherein a primary disazo dye of type—

Phenol←Benzidine→E

is esterified with an arylsulphonyl chloride, has been extended to secondary disazo dyes of the types—



(a) $R^1—SO_2—O—R^2—N=N—$ (with SO_2Y on the ring) $—N=N—E$

where Y = OH, alkyl, aralkyl, etc. and E = γ-acid, 2-amino-8-naphthol-3:6-disulphonic acid, or an *N*-alkyl derivative thereof, whereby violet, blue, or greenish-blue dyes are obtained according to the nature of E[37] and—

(*b*) A Sulphonic acid of aminodiphenyl ether
↓
A Naphthylaminesulphonic acid
(or 2-amino-8-naphthol-3:6-disulphonic acid)
↓
A *para*-coupling phenol esterified with *p*-toluenesulphonyl chloride

whereby orange and red dyes fast to light and washing are obtained[38].

m-Tolidine (2:2′-dimethylbenzidine) has long been employed as a tetrazo component for azo acid milling dyes[39]. More recently *o*- and *m*-tolidines and certain of their derivatives or analogues have been used by Kuhlmann in patents for such dyes. Thus, disazo dyes of greenish- to reddish-yellow hues and good fastness have been obtained from tetrazotised 3:3′-dimethyl-, -dimethoxy-, or -dichloro-4:4′-diaminodiphenyl-6:6′-disulphonic acid with acetoacetarylides as coupling components[40], and neutral-dyeing orange and scarlet dyes for wool and silk from 2:2′-dihalogeno-, -alkyl-, or -alkoxy-benzidines with one molecule of a naphtholsulphonic acid and one molecule of a sulphoarylpyrazolone[41]. E. I. du Pont de Nemours & Co. Inc. have prepared 2:2′-dichloro-3:3′-dimethylbenzidine-5:5′-disulphonic acid for use in both symmetrical and unsymmetrical disazo dyes of excellent fastness properties, with special emphasis on dyes from 1-aryl-3-alkyl-5-pyrazolones. Those dyes having not more than two sulpho groups are said to have good affinity for nylon and to have the same fastness properties on that fibre as on wool[42].

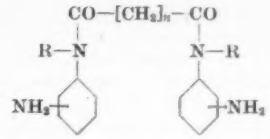
Dye chemists are always on the look-out for the possible application to new dyes of new basic materials of the organic chemical industry. The large-scale manufacture of adipic acid

COOH·$[CH_2]_4$·COOH

for use in making nylon prompted I.C.I. to investigate dicarboxylic acids of this type,

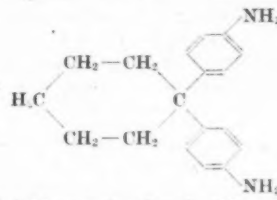
COOH·$[CH_2]_n$·COOH

where n = 1–10, as acylating agents for the preparation of new diamines for use as tetrazo components for acid wool dyes. The acid chlorides were condensed with two molecular proportions of nitro-*N*-alkyl(C_1–C_5)- or -benzyl-anilines, and the bisnitroanilides reduced to symmetrical diamines of general formula[43]—

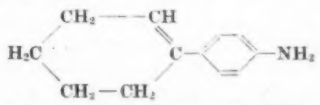


The tetrazo derivatives of the latter when coupled with two molecules of a sulphonated pyrazolone, a naphtholsulphonic acid, or an aminonaphtholsulphonic acid derivative gave dyes of yellow, orange, scarlet, red, and brown hues and good fastness to washing, milling, perspiration, and in many cases also light[44]. Similar investigations were carried out by I.C.I. with benzenedicarboxylic acids as acylating agents (e.g. phthalic and terephthalic acids). The yellow dyes obtained from the tetrazo derivatives of the derived diamines and sulphonated pyrazolone coupling components also had good fastness to wet processing and light[45].

The ready availability of *cyclo*hexanone as a commercial product proved very useful when I.G. prepared some interesting diazo and tetrazo components by reaction, in the presence of an acid, of certain alicyclic ketones or alkyl derivatives thereof with aromatic amines having a free position *para* to the amino group. Condensation products were obtained containing either one or two primary amino groups in the molecule, depending on the proportions of reactants used. I.G. believed the reaction to take place in such a manner that the keto group of the alicyclic ketone reacts with the hydrogen atom in the *para* position to the amino group of the amine used, one molecule of water being split off[46]. Starting with *cyclo*hexanone and aniline, the two types of products of the reaction are represented by the probable formulæ



1:1-Bis-*p*-aminophenyl*cyclo*hexane



4-Amino-2′:3′:4′:5′-tetrahydrodiphenyl

The monoamines can be used as diazo components for yellow to red, violet, and brown dyes from a suitable choice of the usual sulphonated coupling components, and, if desired, they may be reduced to give the fully saturated *cyclo*hexyl derivatives and dyes made from these. These monoazo dyes are said to be distinguished by the purity and brightness of their shades, and by a remarkably good fastness to washing and milling. The dyes containing the fully saturated *cyclo*hexyl ring are said to dye generally yellower than those containing the *cyclo*hexenyl nucleus, the other properties of both groups of dyes being very

similar[47]. The diamines (trinuclear products) can be used as tetrazo components for both symmetrical and unsymmetrical disazo acid milling dyes[48]. For the latter it is an advantage to use the monoxamic acid of the diamine in first making a monoazo dye, which is then hydrolysed, the free amino group diazotised, and the diazoazo compound combined with a different coupling component[49]. This investigation led to the manufacture and marketing of the following members of the I.G.'s range of Supranol milling dyes[50]—

Bordeaux B	Orange G
Brilliant Red 3B	Red 2B
Brilliant Red FB	Red BR

MISCELLANEOUS ACID WOOL DYES

Mono- and di-aminoaryl sulphones have received a good deal of attention in recent years as diazo and tetrazo components respectively. Much of the work has centred around derivatives or analogues of Anthralan Red B (IG)—

2-Aminodiphenyl sulphone $\xrightarrow{\text{Acid}}$ γ-Acid[50]

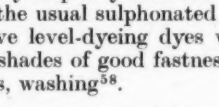
Fast-to-light level-dyeing red to violet dyes are described by Geigy from certain diazotised 2-amino-3′-sulphodiphenyl sulphones coupled in acid medium with γ-acid. The 3′-sulpho group is alleged to have surprisingly good effect on light fastness and to increase the blueness and purity of hue, whilst the level-dyeing properties are substantially unchanged[51]. The same firm have also described the acid coupling of tetrazotised diaminodiphenyl sulphones to γ-acid (two molecules) to give red dyes of high fastness to light and sea-water[52]. Ciba Ltd. have described monoazo red dyes, fast to light and perspiration, from acid-coupled γ-acid and a diazotised aminodiarylsulphone having the amino group *meta* to the sulphonyl linkage[53], whilst Du Pont have patented fast-to-light red dyes from diazotised 2-aminodiphenylsulphones, containing an acylamino or sulphonamido group in the nucleus not containing the amino group, and γ-acid (acid-coupled)[54].

Sulphamyl groups have been widely used as substituents of azo acid wool dyes, usually, apparently, with the object of achieving improved milling fastness. Generally, the amino group of the sulphonamide is substituted at least once by alkyl or aryl. Valuable dyes have been obtained from diazotised aminobenzenesulphonamides and sulphoarylpyrazolones for yellows and acid-coupled γ-acid for fast-to-light reds[55]. The valuable effect of a sulpho group in *ortho* position to the azo group in promoting increased fastness to light has been known for a long time and has been made use of in certain well known commercial dyes, e.g. Lissamine Fast Red B (see above) and Anthralan Orange 2G (IG)[50]. Similar good light fastness results from the use of a substituted sulphamyl group in such a position. Thus, Sandoz have described red dyes of good light fastness from diazotised aniline-*o*-sulphon-alkyl-, -aralkyl-, or -aryl-amides and acid-coupled γ-acid[56]. Level-dyeing blue dyes are said by I.G. to be obtained from the same coupling component and diazotised 4-nitroaniline-2-sulphon-β-hydroxyethylamide[57]. Disazo dyes described by I.C.I.[36], of good fastness to washing and milling, from certain diaminobenzenesulphon-*N*-alkyl(C_1–C_4)- and -benzyl-anilides have already been referred to.

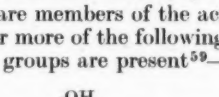
An illustration of the remarkable stability of the sulphonyl fluoride group is provided by the use by I.G. of aminoarylsulphonyl fluorides as diazo components with the usual sulphonated coupling components to give level-dyeing dyes which are said to yield clear shades of good fastness to light and, in many cases, washing[58].

Mordant Wool Dyes

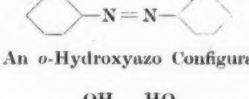
These dyes are members of the acid wool classes in which one or more of the following combinations of substituent groups are present[59]—



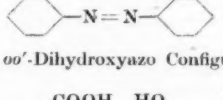
(1) An *o*-Hydroxyazo Configuration



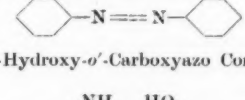
(2) An *oo*′-Dihydroxyazo Configuration



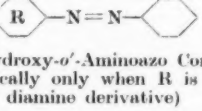
(3) An *o*-Hydroxy-*o*′-Carboxyazo Configuration



(4) An *o*-Hydroxy-*o*′-Aminoazo Configuration (important technically only when R is a *m*-phenylene-diamine derivative)



(5) A Salicylic Acid Residue

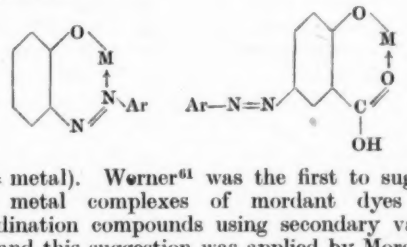


(6) A *peri*-Dihydroxy Configuration

They can be regarded as a special group of acid wool dyes. They may be applied from an acid bath to wool already treated with the metallic mordant (e.g. chrome-mordanted wool), or the metallising, usually with chromium, may take the form of an aftertreatment of the parent dyeing, as with Solochrome (ICI) and Eriochrome (Gy) dyes, representing essentially a two-bath process. Alternatively, the processes of dyeing and metallising may proceed simultaneously in the dyebath, as in what is variously known as the *chromate*, *meta-chrome*, or *monochrome* process. The Solochromate (ICI) and the Synchromate (Ciba) dyes are applied in this way. Finally, the parent dyes may be pre-treated with the appropriate chromium salt and the dye–metal complexes formed in substance. They are then applied to the fibre as acid dyes, although, to secure levelness of dyeing, larger

amounts of sulphuric acid are usually required than with level-dyeing acid dyes. These chromium complexes produce the same light fastness as their counterparts produced by the afterchroming process, but, in general, the resulting dyeings have not such a high degree of fastness to severe washing and milling as the latter. The chief advantage of these chromium complexes, apart from their mode of application, probably lies in their suitability for producing weaker dyeings and brighter hues. The Neolan (Ciba), Palatine Fast (IG), and Ultralan (ICI) dyes are of this type.

Sidgwick[60] pointed out that both *o*-hydroxyazo compounds and azosalicylic acid dyes have configurations permitting the formation of six-membered rings each containing a conjugate double bond, thus—



(M = metal). Werner[61] was the first to suggest that metal complexes of mordant dyes are co-ordination compounds using secondary valencies, and this suggestion was applied by Morgan[62] to the azosalicylic acid and *o*-hydroxyazo dyes. In recent years Drew and his collaborators[63] have thrown much more light on the structures of metallic complexes of azo dyes, particularly the copper and chromium complexes of *oo'*-dihydroxyazo and *o*-hydroxy-*o'*-carboxyazo dyes, whilst Pfeiffer and others[64] have carried out intensive investigations on the stereoisomerism of such complexes, attempting to resolve optically active isomers.

The full fastness required of the technical chrome wool dyes is not obtained from the simple complexes resulting from the action of a chromic salt on a monohydroxyazo compound (type 1 above). Such of these dyes as are employed technically, e.g.—

CARMOISINE W (*C.I.* 179)
p-Naphthionic acid→1-Naphthol-4-sulphonic acid

require a chromic acid compound for development of the shade and fastness properties, and it is presumed that a second *o*-hydroxy group (with respect to the azo group) is introduced. The presence of an oxidising agent, e.g. chromic acid, may be necessary to get the full technically valuable shades even from an *oo'*-dihydroxyazo dye, such as—

SOLOCHROME BLACK PV (*C.I.* 170)
o-Aminophenol-*p*-sulphonic acid→1:5-Dihydroxynaphthalene

The complex on the fibre in such a case was regarded by Morgan as a chromium lake of the hydroxyazonaphthaquinone.

The technical mordant azo dyes for wool are almost all chromium complexes of monoazo or disazo constitution. Apart from some of the yellows, the hues produced in general are not bright. The established yellow and orange dyes of both monoazo and disazo types depend on the use of salicylic acids as coupling components and thus upon the *ortho*-hydroxycarboxylic acid grouping for their chroming properties. Examples are—

SOLOCHROME YELLOW Y (*C.I.* 197)
2-Naphthylamine-6:8-disulphonic acid→Salicylic acid

SOLOCHROME ORANGE GR (*C.I.* 274)
4-Aminoazobenzene-4'-sulphonic acid→Salicylic acid

A salicylic acid residue introduced into disazo dyes A→M→E by means of 5-aminosalicylic acid as diazo component gave rise to useful green and black dyes, e.g.—

DIAMOND BLACK F (*C.I.* 299)
p-Aminosalicylic acid→*α*-Naphthylamine→1-Naphthol-4-sulphonic acid

DIAMOND GREEN B (*C.I.* 302)
p-Aminosalicylic acid→*α*-Naphthylamine→1:8-Dihydroxynaphthalene-4-sulphonic acid

which are both applied to chrome-mordanted wool or by the afterchroming process.

The most important of the technical azo mordant wool dyes are those giving browns and blacks. Of the established dyes the best combination of fastness properties is probably provided by Solochrome Black PV (*C.I.* 170) (see above). It has excellent fastness to light, washing, milling, and potting.

The commercially valuable diazo components for chrome dyes are fairly limited in number. These include the *o*-aminophenolsulphonic acids (e.g. 2-aminophenol-4-sulphonic acid, its 6-chloro- and -nitro-derivatives, and 4-chloro- and 4-nitro-2-aminophenol-6-sulphonic acids), 1-amino-2-naphthol-4-sulphonic acid and its 6-nitro-derivative, and anthranilic acid and derivatives thereof. One or more of these appear in most patents for new chrome dyes, so that recent research on new dyes has largely involved the use of new coupling components or the bringing together of selected known diazo and coupling components for the first time to produce particular effects. Pyrazolones, salicylic acids, hydroxyquinolines, *ortho*-coupling naphthols and their sulphonic acids, and *ortho*-coupling *β*-naphthylamine derivatives and alkaline-coupled aminonaphtholsulphonic acids and their *N*-substituted derivatives are the main types of coupling components employed in the commercial dyes. Search for novelty or improvement continues very largely within these types.

Manufacturers' patents of the last few years for azo mordant wool dyes appear to be designed—

(*a*) to fill in gaps in the ranges of afterchroming dyes (two-bath process) with respect to hue;

(*b*) to extend the number of chromable dyes which develop their full colour value when applied by a one-bath process; or

(*c*) to extend the number of chrome-complex dyes, the use of which also obviates a two-bath dyeing process.

The major target would appear to be (*b*). In this process the dyebath is initially neutral (or faintly alkaline) and contains potassium chromate and ammonium salts. According to Stevens, Rowe, and Speakman[65], as the dyeing and chroming proceed the dyebath becomes more acid, ammonia being evolved. However, work recently reported by R. V. Peryman[66] suggests that in actual fact in large-scale dyeing the bath becomes more alkaline. To be satisfactory for use by the chromate process, a dye must be capable of dyeing from a substantially neutral bath and must not form a

sparingly soluble chromium lake under these conditions. To secure these properties a suitable balance between molecular weight and number of sulpho groups must be preserved. In practice, the best commercial monoazo dyes are found to have not more than one sulpho group, and this is usually in the diazo component.

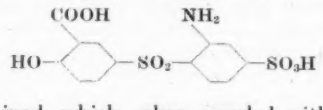
It is most desirable that a chrome dye should develop similar hue, tinctorial strength, and fastness properties when applied by either the one- or two-bath chroming process, so that the needs of the dyer can be met by the minimum number of dyes no matter which method of application is to be used for particular work in hand. It is quite possible that when there are available full ranges of chromate dyes the process of afterchroming will lose some of its present technical importance. This would be the more likely if chromate reds, navy blues, and blacks as cheap as the present afterchrome dyes were found. However, there appears to be no clear-cut road to this goal. A given dye may be quite suitable for application by the chromate process, whilst another, related to it very closely in constitution, may be quite unsuitable.

As regards hues, a good deal of research work has been done in recent years on monoazo dyes yielding greens on chroming. Green is the most widespread hue in nature and the most difficult to achieve with synthetic dyes. Until now it has not been possible to produce mordant dyes giving clear greens from *oo'*-dihydroxymonoazo structures, and it is probably true to say that the problem of obtaining a dye which is equally satisfactory for producing shades of green of high all-round fastness properties by both the afterchroming and chromate dyeing methods has not yet been solved. In this connection, 2-amino-3-naphthoic acid has been a widely used coupling component in patents, Geigy using it with diazo components such as 5-chloro-2-aminophenol-4-sulphonic acid[67] or 4-hydroxy-3-amino-3'-sulphodiphenyl ketone[68] for afterchroming greens. If the parent *o*-amino-*o'*-hydroxyazo dyes are first oxidised to the triazoles before chroming, yellows are obtained[69]. Clear greens of exceptional fastness to light and wet treatments are said by I.G. to be given by the chroming of 6-nitro-2-aminophenol-4-sulphonic acid→2-amino-3-naphthoic acid[70]. Ciba have described dyes, chromable to greens, produced by coupling a diazotised *o*-aminophenol, which may contain a solubilising group, with a β-naphthylamine substituted by an ether group in the 6-position, e.g. 6-nitro-2-aminophenol-4-sulphonic acid→2-amino-6-methoxynaphthalene, chromed (yellowish green)[71]. 5-8-Dichloro-1-naphthol has been used by Geigy for blue and bluish-green metachrome dyes from diazotised 4-chloro- or 3:4-dichloro-5-nitro-2-aminophenol-6-sulphonic acid[72], whilst in a series of Swiss patents I.G. have used 7-nitro-1-amino-8-naphthol-4- and 5-sulphonic acids and 5-nitro-1-amino-8-naphthol-7-sulphonic acid as coupling components for certain nitro-2-aminophenol diazo components to give dyes which yield olive-green hues when afterchromed[73].

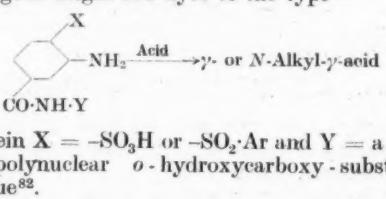
Both diazo (*o*-aminophenol) and hydroxy coupling components containing alkyl groups with more than one carbon atom, or *cyclo*alkyl groups, as nuclear substituents have figured among new components for chrome wool dyes. Presumably the hydrocarbon groups act as weighting groups and tend to make the derived dyes faster to wet treatments and more amenable to dyeing from a neutral bath such as is needed for the chromate process. Thus, Geigy have described the coupling of diazotised 4-alkyl- or 4-*cyclo*alkyl(C_4–C_8)-2-aminophenol-6-sulphonic acids with pyrazolones devoid of sulpho and carboxyl groups to give yellowish-red to bluish-red shades (chromed)[74], and Ciba the use of α-naphthols substituted by alkyl (other than methyl) or *cyclo*alkyl in position 4[75]. Geigy also use 1-naphthol-8-sulphonic acids substituted in position 4 with alkyl-, *cyclo*alkyl-, or aryl-carbonyl or -sulphonyl groups for wine-red to olive-green tints depending on the diazo component used[76], and 2:4-dialkylphenols (e.g. 4-methyl-2-octylphenol) with diazotised 4-nitro-2-aminophenol-6-sulphonic acid for olive–brown chromate dyes[77].

Du Pont have introduced into resorcinol a long-chain alkyl group as part of a nuclear acyl substituent. Dyes from 4-lauroylresorcinol are said to be superior in fastness to washing, milling, and perspiration to similar dyes from resorcinol[78].

Chromable dyes which exhibit little change of hue on chroming always attract interest, and many attempts to obtain such dyes have been made[79]. For this purpose there is usually employed a chromable system, such as a salicylic acid residue, external to the arylazo chromophore. Some years ago British Dyestuffs Corpn. (now part of I.C.I.) proposed to separate the aryl nucleus containing the chelate grouping from the main arylazo chromophore by means of a sulphone $-SO_2-$ or sulphide –S– bridge[80]. Thus, by condensing sodium 5-sulphinosalicylate with 1-chloro-2-nitrobenzene-4-sulphonic acid and reducing, the amine—



was obtained, which, when coupled with phenylmethylpyrazolone, gave a yellow dye which retained its hue on chroming. The corresponding dye from acid-coupled γ-acid is Diamond Red 3B (IG)[81]. Geigy have recently described somewhat analogous bright red dyes of the type—



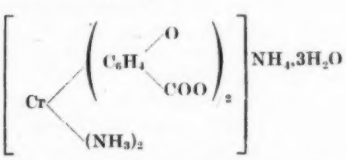
wherein X = $-SO_3H$ or $-SO_2\cdot Ar$ and Y = a mono- or polynuclear *o*-hydroxycarboxy-substituted residue[82].

I.C.I. have carried out a considerable amount of research in recent years on dyes for application by the one-bath chroming process, as revealed by a series of patents in their name. They have used 1-diphenylyl-3-(methyl or phenyl)-5-pyrazolones[83] and 1-phenoxyphenyl-3-(methyl or phenyl)-5-pyrazolones[84] as coupling components for orange–brown to bluish-red chromate dyes of good fastness

to washing, milling, potting, and light. 1-Phenyl-5-pyrazolone-3-carboxyamides, in which one hydrogen atom of the amide group is replaced by a single substituent, which is either a phenyl radical carrying one or more halogen substituents or is an α-naphthyl radical, have been used for similarly fast bordeaux dyes[85]. 1-(3′:4′-dichlorophenyl)-3-methyl-5-pyrazolone was used for orange to red dyes[86]. The diazo components in all these cases were various *o*-aminophenol- or *o*-aminonaphthol-monosulphonic acids. I.C.I. have also described a black chromate dye in 4-nitro-2-aminophenol-6-sulphonic acid→6-bromo-2-naphthol[87].

The *N*-acyl derivatives of 1-amino-8-naphthol-6-sulphonic acid, to which reference has already been made in connection with acid wool dyes, have been used by I.G. as coupling components for chromable dyes[88]; the chromed dyeings are said to be more level than those from *N*-acyl derivatives of 1:8 aminonaphtholdisulphonic acids, and to be full and bright blues as compared with the reds or otherwise feeble dyeings obtained from corresponding derivatives from 1:8-aminonaphthol-4- and -5-sulphonic acids. *N*-Acyl derivatives of 1:6:3- and 1:3:6-aminonaphtholsulphonic acids have also been used as coupling components for red, grey, violet, and black dyes. The parent acids are obtained by caustic fusion of 1-aminonaphthalene-3:6-disulphonic acid, whereby a mixture of the aminonaphtholsulphonic acids is obtained, the components of which can be separated by means of the different solubilities of their salts[89]. 2-Acetylamino-6-naphthol-8-sulphonic acid is the coupling component employed for Eriochrome Greys 3BL and 3GL (Gy)[90].

For the production of chrome complexes in substance Geigy have described the use as chroming agents of chromium complexes of salicylic acid and its derivatives[91]. An example is ammonium chromium salicylate. Barbieri[92] has described such complexes and assigned to ammonium chromium salicylate the structure—



Geigy state that mild reaction conditions are employed with such an agent, so that side-reactions, especially hydrolysis of amide or ester groups, are avoided. Moreover, the derived chromed dyes are said to give full and level dyeings from a mildly acid dyebath, in contrast to existing dyes of this type (Neolan, Palatine Fast, and Ultralan), which require a high concentration of sulphuric acid for satisfactory dyeing. Examples of parent dyes used include *o*-amino-phenol or -naphthol→1-naphthol-8-sulpho-3- or 5-sulphonamides.

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MIDLANDS SECTION

Meeting held at the Victoria Station Hotel, Nottingham, on 9th March 1949, Mr. D. B. McPherson in the chair

Dyeing and Finishing Mixtures containing Acetate Rayon Staple Fibre

A. Mellor and H. C. Olpin

Introduction

Spun-rayon mixture fabrics are assuming a new importance in the textile world. They are not new, but only during recent years have they received the attention that is their due, and been proved to have their own peculiar merits.

With their inherent advantage of accurate control in manufacture to suit the intended use, the rayon staple fibres were early recognised as valuable partners for the natural fibres—not displacing them, but supplementing them by broadening and diversifying their field of use.

Even before the war much valuable development work had been done to make full use of the advantages offered by fabrics constructed from blended fibres, not the least of which was the versatility of coloration which could be achieved on the grey fabric in the hands of the dyer.

Usually two fibres only are present in blended yarns and fabrics, but occasionally a wider combination is used to produce speciality and novelty effects. The 85–15 and 50–50 viscose–acetate blends are established favourites, but there is every indication that acetate–wool will prove equally popular when more spinning capacity is available. The acetate–wool fabrics already produced have shown that desirable lightweight suitings can be made, whose properties and value entitle them to consideration beside the traditional all-wool types.

Of these mixtures the 50–50 acetate–viscose is the most important, large quantities being produced in this country and still larger quantities in the U.S.A.

Given correct balance and construction, coupled with correct dyeing and finishing conditions, fabrics of outstanding merit can be produced. Careful consideration is required when building up yarns and fabrics, and attention must be paid to such physical characteristics as staple length, denier, and twist, since these affect the strength and evenness of yarn, and unless correctly balanced may cause all kinds of trouble in processing.

Cellulose acetate fibre in admixture with viscose fibre will give a resiliency and resistance to creasing which is not obtainable in a 100% viscose fabric unless an additional non-crease finish is applied. On the other hand, viscose in such a blend gives improved resistance to ironing as compared with 100% acetate material. Again, cellulose acetate has a specific gravity almost identical with that of wool (1·35), and so it is a very suitable fibre for mixing or blending with the latter. It will be found that a wool–acetate blend has insulating properties equal to those of 100% wool, whilst in addition the presence of acetate will appreciably reduce the tendency to felting during processing and subsequent laundering.

The scouring, dyeing, and finishing of these fabrics present ample scope, and quite often past experience and knowledge will dictate the method of approach and the type of handle and finish given.

The removal of sizing material and the release of weaving and spinning strains are the first essentials, and such initial treatment can have a most important bearing upon the final finished handle and appearance. For example, should the grey or raw fabric be reedy, and be processed with warp tension during the first wet operation, it is more than likely that the final fabric will lack the cover and the fullness of handle desired. It is therefore necessary to ensure that maximum relaxation be permitted during the initial scour, and any method which will assist the fibres and yarns in taking a stable position without causing creases should be encouraged. There are two methods which might

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be referred to here which have as their aim the achievement of full handle coupled with final stability.

Improved cover and stability can be obtained with a 50–50 acetate–viscose staple fabric sized with starch, if this is given its initial desizing treatment by processing in a drum, so that the fabric is tumbled about at the maximum temperature which will not destroy the starch-removing enzyme, e.g. for 30 min. at 60°c.

The second method of appreciable assistance in the elimination of reediness is to run the fabric through a pad-mangle fitted with rollers covered with porcupine rubber. In this way a gentle kneading action is applied, so assisting the natural redisposition of the warp threads when the weaving strains are being released during the initial wetting.

The successful dyeing of mixture fabrics demands a thorough knowledge of the chemical and physical properties of both dyes and fibres, so we will now examine in more detail the processing of, first, the acetate–viscose staple types, and then the acetate staple–wool fabrics.

References to *Celafibre* in this paper are to the brand of cellulose acetate staple fibre sold by British Celanese Ltd. under this registered trade mark.

The present paper is concerned mainly with dyeing in the fabric form. Therefore we do not propose to discuss the possibilities of blending dyed stocks, attractive as they are from the point of view of fastness when coloured by means of pigments incorporated in the spinning dope. Nor do we consider that blending such pigmented fibres with undyed fibres is particularly attractive, since the general fastness will be governed by that of the cross-dyed fibre; also the added cost of the pigmented fibre and the necessity for keeping a multiplicity of stocks would more than outweigh the small advantage gained. These remarks do not, of course, apply to the use of coloured yarns as effect threads.

Celafibre–Viscose Staple

The pretreatments essential in the processing of Celafibre–viscose staple fabrics are simple, and consist essentially in removing the size and lubricants used in the manufacture of the fabric.

Many sizes in use at the present time are based on starch, and therefore treatment with suitable enzyme or malt solutions will be required. This pretreatment can be given on the dye jigger by running the fabric two ends through 1% malt solution at pH 6–7 and 60°c., using minimum tension. The fabric can then be transferred to the winch for washing off and dyeing.

There is not much to be said about the dyeing operation proper, except to point out that as little tension as possible should be permitted, the winch speed should be about 60 linear yards per minute, and the fly roller preferably mounted on ball bearings so that as little drag as possible is exerted at this point.

It has been noticed that some of the heavier fabrics, because of their greater holding capacity for water, lie flat on the winch and show little tendency to open out when immersed in the shallow baths now so often used for continuous-filament fabrics. It is suggested that in these cases a return to the deeper machines will be an advantage, for then these fabrics can sink and so have a better chance of changing folds, which should assist levelling. In any case, levelling is usually quicker and simpler with Celafibre–viscose staple mixtures than with 100% materials, because of the lattice effect of the individual fibres in such mixtures. Incidentally, this remark applies also to Celafibre–wool mixtures.

VISCOSE STAPLE DYED–CELAFIBRE RESIST

This style undoubtedly gives very attractive colorations, the element of variety introduced by the blending adding to the interest of the finished product. Either during spinning of the yarn or during dyeing, the Celafibre has a tendency to ride to the surface of the yarn, so that it is more in evidence than the viscose staple. This is a limiting factor, for when the Celafibre only is dyed, a much darker or fuller shade is apparent than when the viscose staple only is dyed, and this in spite of the initial 50–50 blend being satisfactory.

The necessity for dyeing full shades on the viscose staple, leaving the Celafibre quite white, somewhat narrows the field for selection of dyes. Direct cotton dyes can be used, fast-to-washing effects being obtained by diazotising and coupling, but vat dyes and azoics must be ruled out for full shades owing to excessive staining of the Celafibre, though both may be used for solid shades or cross-dyed effects. Resist dyes in the direct cotton range are so well known that everyone is fully conversant with them or can easily obtain details from any dye manufacturer.

BOTH CELAFIBRE AND VISCOSE STAPLE DYED

Whether solid or cross-dyed effects are required, this technique has been established so long on acetate–viscose mixtures that detailed instructions for procedure would be superfluous. Certain points, however, may be of sufficient interest to merit discussion.

SOLID SHADES — Imperfections in blending, which in resist styles are not objectionable and may indeed be contributory to the effect, demand exact matching on both fibres if best results are to be achieved in solid shades.

One of the difficulties in dyeing solid shades on 50–50 mixture fabrics arises during matching, for given a good blend it is almost impossible to tell which fibre is responsible for the divergence of the shade from the required standard, and the dyer is at a loss to know whether to add dye for the acetate or the viscose staple, or wool if that is the other fibre.

The simplest way out of this difficulty is to run with samples of 100% acetate and 100% viscose fabric in the dyebath and take samples from these in addition to those from the batch, so that the effect of the last dye additions can be seen. These samples or test fabrics should consist of fibres as closely similar as possible to those of the fabric in work. Naturally the final pass-off is judged on the sample taken from the batch. It is not advisable to rely on these controls for matching purposes,

since several factors may intervene to militate against their exactly matching the respective components of the fabric.

Sometimes extraction of the cellulose acetate with acetone can be used to reveal imperfections in the blending, and the irregularities can then be covered by good colour matching; certainly poor matching will accentuate blending unevenness.

Mixtures of dispersed and direct cotton dyes are satisfactory for many purposes, and the only shades needing comment are black and navy blue. The former is obtained with a mixture of SRA Fast Black IV, Chlorazol Black E extra or LF, and Chlorazol Blue BH.

Navy Blue is interesting since, although it is true that diazotisable bases may be applied to both fibres, the result of simultaneous diazotisation and coupling with 2-hydroxy-3-naphthoic acid is not satisfactory from the aspect of fastness to alkali and light. Very satisfactory results are obtained, however, by the use of SRA Navy Base VI and a blue of the Diazo Indigo Blue BR type, both of these coupling with SRA Navy Developer I or SRA Developer 437, both of which are arylamines, to give navy blues of superior all-round fastness. This technique can be extended to other full shades if necessary.

Details of processing are given below.

SOLID BLACK ON 50–50 CELAFIBRE–VISCOSE STAPLE OR THE LIKE

The previously prepared and scoured goods are dyed in the usual manner with the following recipe—

4%	...	SRA Fast Black IV base 300 powder (BrC)
3%	...	Chlorazol Black E extra or LFS (ICI)
1%	...	Chlorazol Blue BH (ICI)

calculated on the total weight of the fabric.

Enter at 40°C., raise to 75°C., add 5 g. sodium sulphate or common salt per litre, and continue dyeing until the viscose staple is sufficiently well dyed. The goods are well washed off.

DIAZOTISATION— The previously dyed and washed goods are treated for 30 min. at 20°C. in a bath containing per litre—

1·5 g.	...	Sodium nitrite
6·0 c.c.	...	Hydrochloric acid (28° Tw.)

and then adequately rinsed with cold water.

DEVELOPMENT— The diazotised goods are entered into a developing bath containing per litre—

0·5 g.	...	2-Hydroxy-3-naphthoic Acid
0·5 g.	...	Brenthol AT (ICI) (Naphtol AS–G)
0·8 g.	...	Caustic soda

the liquor : goods ratio being 20 : 1. The developers are dissolved in hot water containing the requisite quantity of caustic soda, and added to the bath, which has been previously set with (per litre)—

1 c.c.	...	Dispersol VL or the like
1·2 c.c.	...	Formic acid (85%)

The goods are entered cold, and the temperature is raised to 60°C. in 30 min. and maintained at 60°C. for 20 min. This treatment is followed by a warm rinse and finishing as requisite.

SOLID NAVY BLUE ON 50–50 CELAFIBRE–VISCOSE STAPLE OR THE LIKE

The previously prepared and scoured goods are dyed in the usual manner with the following recipe—

1–2%	...	SRA Navy Base VI 300 powder (BrC)
3–6%	...	Paramine Diazo Blue BR (LBH)

according to depth of shade required, calculated on the total weight of fabric.

Enter at 40°C., raise to 70°C., and add 5 g. sodium sulphate or common salt per litre, dyeing being continued until the viscose staple is sufficiently well dyed. The goods are washed off.

DIAZOTISATION— The previously dyed and washed goods are treated for 40 min. at 25°C. in a bath containing per litre—

1·5 g.	...	Sodium nitrite
6·0 c.c.	...	Hydrochloric acid (28° Tw.)

and then adequately rinsed until the pH of the bath is 6·5–7·0.

DEVELOPMENT— The diazotised goods are entered into a developing bath containing per litre—

0·1 g.	...	Sodium acetate
0·1 g	...	Glacial acetic acid
0·8–1·6 g.	...	SRA Navy Developer I paste (according to amount of base)

The requisite quantity of developer is warmed with an equal weight of Dispersol VL or the like, and diluted with warm water before being added to the developing bath. The temperature is raised to 60°C. in 20 min. and maintained there for 30 min. Finally the goods are rinsed and given a light soaping.

CONTRASTING SHADES— These are achieved by the same technique as solid shades. It is equally essential to use dyes of optimum resist properties when maximum contrast is desired, as when dyeing fabrics one way only. Although direct dyeing dyes will normally be used for both fibres, it should also be mentioned that it is possible to obtain quite a wide variety of contrasting shades by diazotising and developing simultaneously on both fibres.

(Samples of Celafibre–viscose staple yarn in hank form in resist, solid, and two-colour effects were exhibited.)

FINISHING

After dyeing, hydroextraction is usually given by a passage over the suction dryer. Cool drying on a brattice type of machine is the most satisfactory method, but excellent results can be obtained on the pin stenter, using as much overfeed as will yield the correct balance between the warp and weft coupled with the necessary fullness of handle and satisfactory draping properties.

One of the principal objectives in finishing is the production of cloth with good stability, and the accepted standard for a non-shrink fabric is that it shall not show more than 2% shrinkage in either warp or weft direction.

It is not desirable to push this overfeeding so far that fabrics extend during wear, for this fault is far more objectionable than a slight shrinkage, which can often be recovered during ironing.

The non-crease resin finish, now in frequent use for viscose staple fabric, is not a necessity with 50–50 Celafibre–viscose staple mixtures; this finish can, however, be used with advantage in the appropriate amounts to give finishes of a crisp or firm character.

Many Celafibre–viscose staple fabrics are given a singeing process prior to scouring, and so they are usually clean and free from excessive surface fibre when they arrive in the finishing room. In such cases the finisher will give a very light raising, followed by steaming and decatising.

If, however, a particularly full warm finish is required, the singeing process should be omitted, and any exceptional or irregular hairiness removed instead by cropping.

For suitings, a single passage through a continuous press of the Hattersley Pickard or Berry type is often given, but a better and fuller handle is obtained if the fabric is simply folded in hot paper and left stacked under its own weight overnight.

Gas Fading on Celafibre Mixture Fabrics

Susceptibility to gas fading of certain of the dyes at present in use on the Celafibre content of these mixtures must, of course, be recognised; and for so long as it remains necessary to use these dyes, protective measures must be taken. Two of the most effective treatments for all-Celafibre goods are—

(1) Triethanolamine, applied as a finish, about 1% on the weight of fabric being used; and

(2) 1% Methylolmelamine (obtainable as proprietary products), also applied as a finishing process, curing being desirable to effect polymerisation.

The former of these treatments is effective only till the goods are washed, but the latter is wash-fast if curing is carried out satisfactorily. These finishes have no adverse effect on non-ionic dyes such as vat and azoic, and may safely be used in

conjunction with them, but sulphonated dyes are all more or less severely affected as regards fastness to light. It is therefore necessary to make sure that dyeings with direct cotton dyes, for example, are of sufficient fastness after such treatment. A practical alternative which avoids this difficulty is to dry in, say, 1% of an inorganic alkali such as borax, which affords adequate protection without loss of light fastness.

The substantive inhibitors, being absorbed selectively by the Celafibre along with the dispersed dyes, do not adversely affect light fastness on the viscose present, and being of the same order of fastness to washing as the dispersed dyes, come under consideration.

At this point it may be worth while to set out the desirable properties of the ideal inhibitor. It must be—

(1) Substantive to cellulose acetate but not to other fibres, and applicable simultaneously with the dye

(2) Fast to washing and dry cleaning, i.e. comparable in this respect with the usual dispersed-type dyes

(3) Colourless

(4) Odourless

(5) Non-volatile

(6) Basic in character, i.e. more basic than the dyes to be protected, but not sufficiently to cause saponification

(7) Fusible above 100°C., i.e. it must remain solid in the dyebath under all conditions

(8) Not discoloured on exposure either to light or to an atmosphere containing oxides of nitrogen

(9) Must not affect the fastness of dyes on cellulose acetate or other fibres present

(10) Cheap

This is a formidable list, and there is no inhibitor available to-day that passes every one of these tests satisfactorily. A compound which loses least points when judged against these desiderata is diphenylacetamidine[1], though unfortunately it is not so basic as one would wish. Its freedom from discoloration on exposure to light or gas fumes is a matter of importance when used to protect pale shades.

Certain arylamines, particularly the alkylated arylamines, have been proposed from time to time. but they suffer, without exception, from the defect of discoloration on exposure. During the past few years diphenylethylenediamine, which will be recognised immediately as belonging to this group, has been placed on the market in America under the name Anti-fume D.E. (Du Pont) and has recently appeared on the British market as Duranol Inhibitor GF (ICI). It is interesting to compare the properties of this compound with those of the first mentioned substantive protective agent (Table I).

Other pairs of inhibitors could have been chosen for this comparison, but diphenylacetamidine and diphenylethylenediamine between them seem to possess most of the desirable characteristics of a substantive inhibitor. The problem of embodying them in one compound cannot long evade solution.

TABLE I

	Diphenylacetamidine	Diphenylethylenediamine
Constitution ...	$CH_3{\cdot}C(:N{\cdot}C_6H_5){\cdot}NH{\cdot}C_6H_5$	$C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C_6H_5$
(1) Substantivity ...	Both substantive to acetate, but not to cellulose or wool	
(2) Fastness to washing	Both resist moderate laundering	
(3) Colour	White	White
(4) Odour	Not detectable at 1% on wt. of goods	
(5) Volatility ...	Non-volatile	Non-volatile
(6) Basic properties (equiv. wt.	Monacid base 210	Diacid base 106)
(7) Melting-point ...	130–133°c.	66°c.
(8) Discoloration ...	Does not discolour	Slight browning on exposure to light Becomes yellow in S.D.C. gas fumes test[2]
(9) Effect on fastness to light	Slight protective action; direct cotton dyes unaffected	Discoloration of protective agent noticeable on certain shades
(10) Cheapness ...	Both products can be made from cheap and readily accessible intermediates	

Celafibre–Wool

The initial processes applied to Celafibre–wool fabrics are concerned with the removal of lubrication applied during the yarn and fabric manufacture, and the release of weaving or knitting strains so as to give stability.

Scouring in soft water with soap is still the preferred method for removal of dirt and oil, but with some fabrics it is preferable to give a mild crabbing process prior to scouring, so as to obtain stability to shrinkage and distortion during subsequent scouring and dyeing.

WOOL DYED–CELAFIBRE RESIST

This is a definite trade requirement, and is the easiest style to execute, requiring only dyes having good resist properties for the Celafibre. (*Illustrative samples were shown.*) Acid or chrome dyes are used according to the type of work and fastness required, the following being typical procedures—

The acid dyes are applied from a Glauber's salt–acetic acid bath, exhausting with formic or sulphuric acid as requisite for the individual dyes.

The following dyes, all of which have good Celafibre resist properties, are typical—

Coomassie Yellow GS	ICI
Coomassie Yellow RS	ICI
Coomassie Blue BLS	ICI
Coomassie Brilliant Blue BS ...	ICI
Naphthalene Scarlet BS	ICI
Merantine Blue BF	LBH
Elite Fast Red G	LBH
Brilliant Milling Blue R	LBH
Xylene Light Yellow 2G	S
Xylene Fast Orange G	S
Azo Rubinole 3GS	S
Brilliant Sulphon Red B	S
Xylene Fast Green B	S
Alizarin Direct Brown BL ...	S
Azo Acid Black FL	S
Cloth Fast Yellow 2G	CAC
Cloth Fast Orange R	CAC
Cloth Fast Red B	CAC
Cloth Fast Brilliant Blue 2B ...	CAC
Cloth Fast Blue B	CAC
Cloth Fast Green G	CAC
Cloth Fast Black 4BN	CAC
Polar Yellow 3G	Gy
Polar Red 3B...	Gy
Polar Red Brown V	Gy
Polar Orange GS	Gy

The Neolan (Ciba) dyes, closely allied to the above group in method of application, offer fastness

properties of a high standard together with good resist properties. They are applied as for all-wool goods from a sulphuric acid bath, but with the temperature restricted to 80–85°C.

Application of the chrome dyes (usually afterchrome) also closely follows the procedure generally used for all-wool goods, viz. from an acetic or formic acid bath, exhausting where necessary with sulphuric acid and chroming in the exhausted dyebath with the amount of dichromate requisite for the particular depth of shade. It has been observed that where some staining has occurred when using afterchrome dyes, a noticeable clearing or improvement of shade of the acetate takes place during the afterchrome treatment. The following are typical examples of the range of dyes—

Chromosol Yellow GD	S
Chromosol Yellow GR	S
Omega Chrome Orange R	S
Omega Chrome Orange G	S
Omega Chrome Brilliant Blue B ...	S
Omega Chrome Green F	S
Solochrome Flavine GS	ICI
Solochrome Yellow 2GS	ICI
Alizarine Red AS	ICI
Omega Chrome Red G	S
Solochrome Red BS	ICI
Solochrome Cyanine RS	ICI
Solochrome Brilliant Blue BS ...	ICI
Solochrome Green VS	ICI
Acid Alizarine Black ST	LBH
Eriochrome Yellow G	Gy
Fast Chrome Blue CR	Gy
Metomega Chrome Yellow ME ...	S
Metomega Chrome Brown DNE ...	S
Metomega Chrome Cyanine BLL ...	S
Metomega Chrome Green BLL ...	S
Metomega Chrome Green GL ...	S

CELAFIBRE DYED–WOOL RESIST

This is not a practicable style owing to the staining of the wool by dyes suitable for the Celafibre. However, since this subject has some considerable significance when dyeing solid shades, it would not be out of place to consider it as a separate item. The only class of dyes coming under consideration for this mixture is the dispersed type, other types such as the Solacets (ICI) being ruled out owing to their great affinity for wool.

The dispersed-type dye which stains the wool is almost always fugitive to light on that fibre, so that it becomes a matter of considerable importance to reduce this staining to a minimum. This calls for detailed study of dyebath conditions and for careful selection of dyes staining least under optimum conditions. In making this study we have used separate cellulose acetate and all-wool fabrics for greater clarity and ease of interpretation of the results. We have used the S.R.A. range because naturally we are more familiar with it, but our remarks are applicable to dispersed-type dyes in general.

The intensity of staining was found to be dependent on a number of factors, which will be discussed individually—

1. pH OF DYEBATH— The importance of pH control was illustrated by dyeings carried out for 2 hr. at 80°C. as follows—

The dyebaths were set with 2 c.c. Dispersol VL per litre and 4% SRA Brilliant Blue IV 300 powder (previously dispersed) based on the weight of cellulose acetate. Additions to control the pH of the individual baths are indicated in Table II.

TABLE II

	pH	Dyebath Addition (per litre)	Staining of Wool Resist
(1)	3	5 g. Sodium sulphate 0·4 g. Sulphuric acid	Strong
(2)	5	5 g. Sodium sulphate 1 g. Ammonium acetate	Fair
(3)	7	5 g. Sodium sulphate	Fair to slight
(4)	9	0·5 g. Soda ash	Very slight (some yellowing of the wool)

2. INFLUENCE OF DYEING TIME— A full brown was chosen for test, and the following dyebaths and dyeing conditions were used—

42 g. of cellulose acetate and 18 g. of wool (the latter cut into five swatches) were entered into a two-litre bath containing—

2·3% SRA Golden Yellow IX 300 powder
4·5% SRA Fast Red FSI 300 powder
1·3% SRA Brilliant Blue IV 300 powder

on the weight of cellulose acetate and

2 c.c. ... Dispersol VL
5 g. ... Sodium sulphate
1 g. ... Ammonium acetate

per litre. The bath was heated to 80°C. and the cellulose acetate and wool were entered, a swatch of wool being removed from the bath after 5, 30, 45, and 90 min. respectively. The reduction of staining of the wool was evident as dyeing proceeded. The dyebath conditions given above have been found to be optimum for minimum staining of the wool with the dispersed-type dyes, *whilst still retaining the necessary pH to ensure exhaustion* of the acid dyes on the wool.

3. DYE SELECTION— Having established the importance of the above two factors, we then examined a number of dyes applied under optimum conditions, our assessments being given in Table III.

TABLE III

Dye	Type	Staining
SRA Pure Yellow III ...	Nitroarylamine	Slight to fair
Eastman Yellow GLF ...	Nitroarylamine	Very slight
SRA Golden Yellow IX ...	Nitroarylamine	Slight to fair
SRA Fast Golden Yellow FSI	Nitroarylamine	Fair to moderate
SRA Fast Red VII ...	Anthraquinone	Fair to moderate
SRA Fast Red FSI ...	Anthraquinone	Fair
SRA Red VIII	Nitroaminoazo	Strong
SRA Rubine IX	Nitroaminoazo	Strong
SRA Fast Violet II ...	Anthraquinone	Slight to fair
SRA Fast Blue III ...	Anthraquinone	Slight to fair
SRA Brilliant Blue IV ...	Anthraquinone	Slight to fair
SRA Fast Blue FSII ...	Anthraquinone	Slight to fair

A useful all-purpose selection taken from Table III would be—

SRA Golden Yellow IX
SRA Fast Red FSI
SRA Brilliant Blue IV

Where maximum light fastness is required SRA Fast Golden Yellow FSI and SRA Fast Blue FSII should be substituted.

To summarise— control of the dyebath pH at 5–7, adequate dyeing time to ensure clearing of wool as dyeing proceeds, and careful selection of dyes, avoiding those of the nitroaminoazo group, which stain most, are all important factors in reducing staining of the wool to a minimum.

BOTH CELAFIBRE AND WOOL DYED

From the foregoing discussion on the staining of wool by dispersed-type dyes it will be appreciated that the technique used for cross-dyed effects must ensure maximum freedom from such staining. Two courses are therefore available—

(1) To dye the wool with dyes of sufficient fastness to withstand cross-dyeing with dispersed-type dyes from a slightly alkaline dyebath at 80°C.

(2) To use a single-bath method, the dyes for the wool being limited to those having good affinity and adequate fastness properties when applied simultaneously with the dispersed-type dyes.

Chrome-mordant dyes are satisfactory for the first procedure, and good results can thereby be obtained, but since double processing rarely appeals to the dyer when single-bath methods are available, we shall discuss the second procedure. There is a fairly adequate range of neutral-dyeing acid dyes which are admirable with respect to both shade building and fastness properties. Many members of the following well known ranges are useful—

Carbolan	...	ICI	Cloth Fast		CAC and Ciba
Coomassie	...	ICI	Xylene		S
Polar range	...	Gy	Xylene Milling		S

and the following individual dyes—

Chlorazol Fast Red FS	...	...	ICI
Solway Rubinole RS	...	...	ICI
Elite Fast Red G	...	...	LBH
Brilliant Milling Blue R	...	...	LBH
Brilliant Milling Blue G	...	...	LBH

This list is intended only to serve as an indication of the type of dye which is satisfactory.

As mentioned above, it is essential to allow adequate time for a dispersed-type dye which stains the wool in the initial stages of dyeing to be transferred to the Celafibre. It is equally desirable, though this necessarily follows, that the smallest amount of dye which will give the required shade should be used.

CHLORINATION FOR STABILISATION

The admixture of Celafibre with wool tends to inhibit felting, and so, for these Celafibre–wool fabrics, there is not the same need or inducement as with pure wool to resort to chlorination in order to prevent shrinkage. In any case, Celafibre–wool fabrics are easier to process by chlorination than wool–cellulose, since there is less risk of degradation. As the presence of acetate goes part way to producing a stable finish, the safe recommended process for treating the wool in order to give still better resistance to shrinking will be the enzyme or papain process covered by a Wool Industries Research Association patent[3] and available to licensees.

If, however, chlorination is still preferred and chlorinated wool has not been used in the initial blending, then wet chlorination, using fairly heavy pad-mangle nip rollers to ensure even and thorough penetration of the chlorine liquor is the preferred process.

To assist in obtaining stability it is recommended that during scouring some squeezing or light milling be given. Such a process will help warp shrinkage, which normal processing on a machine designed for rayon tends to retard.

Conclusion

In this brief survey of a subject which embraces several fibres and many fabrics, and offers a very wide field for the exercise of the skill of the dyer and finisher, we have indicated what appears to us to be the main considerations in processing goods containing acetate staple fibre. We have dealt at some length with the questions of the staining of wool by dispersed-type dyes and of gas fume fading, because information on these two points is not readily available in the technical literature.

The authors thank Messrs. British Celanese Ltd. for permission to publish this paper.

References

[1] Imperial Chemical Industries Ltd., *B.P.* 547,893.
[2] J.S.D.C., **64**, 134 (April 1948).
[3] Wool Industries Research Association, *B.P.* 513,919.

Discussion

Mr. F. M. STEVENSON: In the exhibited dyeings of solid shades on wool–Celafibre, the pieces of 100% wool included in the test are invariably darker than the corresponding pieces of 100% acetate, yet the mixture pieces dyed with them appear perfectly solid. Is there any reason for dyeing the wool a darker shade?

Mr. OLPIN: The deeper the shade on the wool the more effectively will the looseness to light of the staining of the dispersed-type dye be covered. Apart from this, it is usual and permissible to dye the duller fibre a slightly deeper shade.

Mr. W. PENN: What is the best temperature for dyeing wool–Celafibre solids?

Mr. MELLOR: We are of the opinion that 80–85°C. is best, because the exhaustion of the dyebath at this temperature is usually quite good, whilst there is also less risk of creasing than at higher temperatures.

Mr. E. E. BOWKER: The samples exhibited of the staining of wool by dispersed-type dyes have faded badly, but the staining is very much lighter than the shade of acetate with which it is exposed. Would the fading of acetate dyed to such a pale shade not be equally rapid?

Mr. OLPIN: The staining on wool is very much looser to light than the corresponding depth on Celafibre.

Mr. A. S. CLULEY: It has been mentioned that spinning acetate staple with wool inhibits shrinkage of the latter, but there may be occasions when a milled effect is desirable. What are the lecturers' recommendations?

Mr. MELLOR: Should circumstances arise which make it desirable to obtain a milled effect on acetate–wool blended fabrics, the only process known to the lecturer is that covered by a patent taken out by Professor J. B. Speakman, in which phenol or other suitable swelling agent for the acetate is used as an assistant in the milling operation (British Celanese Ltd., Speakman, and Crummett, *B.P.* 519,708, 591,712, and 609,370).

Mr. CLULEY: Is the fastness to perspiration of dispersed-type dyes on wool–Celafibre satisfactory for men's half-hose?

Mr. OLPIN: The dispersed-type dyes are quite satisfactory on the Celafibre portion. Fastness on wool should reach established standards if suitable dyes are chosen.

Mr. CLULEY: There is a market for men's tropical suitings of acetate–Fibro (Courtaulds). Do the lecturers recommend winch or jig dyeing?

Mr. MELLOR: Processing on the winch is the preferred method of dyeing tropical suitings, since thereby better stability and fullness of handle can be obtained.

Mr. C. W. EDWARDS: Why do the lecturers prefer the enzyme process for shrink-resisting wool–Celafibre? We have processed considerable quantities of wool–acetate with a controlled acid chlorination and have observed no shortcomings whatever.

Mr. MELLOR: Fabrics made from wool–acetate blended fibres are normally resistant to shrinkage, but if additional safeguard is required the enzyme process can be recommended because it appears to be safe and under complete control the whole time, it gives sufficient additional stability to the wool, and standard equipment can be used for its application.

Mr. EDWARDS: What is the optimum percentage of acetate in a wool–Celafibre mixture from a shrink-resist standpoint?

Mr. MELLOR: Most of our trials have been carried out on fabrics made from 70–30 wool–acetate blended yarns. These give substantially greater resistance to shrinkage than 100% wool. It is considered that, as the proportion of acetate is increased in these blended fabrics, the resistance to shrinkage will increase, too.

Mr. W. PENN: What precautions are necessary to avoid a "papery" handle in dyeing Celafibre–Fibro on the jigger?

Mr. MELLOR: A dye jigger fitted with easy-running jig rollers and with guide rollers mounted on ball bearings is considered desirable for mixture fabrics which must be processed in open width. Running with minimum tension is essential and to assist in achieving this end, the batch size should be kept as small as is economically possible, say 350–400 yd.

LONDON SECTION

Meeting held at the George Hotel, Luton, on 8th April 1949, Mr. H. A BRASSARD in the chair

Felt Dyeing and Processing

B. KRAMRISCH

Before dealing with certain aspects of felt dyeing and processing, it is of interest to make some reference to the factors which determine felting and to the theories which have been put forward to account for the behaviour of animal fibres during the felting operation.

This subject has been studied in detail by Speakman and his colleagues at Leeds University, and by Martin and other workers at the Wool Industries Research Association. Problems directly connected with the hatting industry are now being investigated at the British Hat and Allied Felt-makers' Research Association.

A critical review of the nature of felting has been made by Freney[1]. A widely accepted view involves a directional frictional effect (D.F.E.); i.e. it postulates that when animal fibres are subjected to frictional forces, as in milling, they always travel in one direction, viz. towards the root end of the fibre. This behaviour has been shown to be due to the characteristic manner in which scales are placed on the surface of the fibre[2].

Felting properties of animal fibres are in general governed by the following factors—

(1) Characteristic surface scale structure
(2) Ease of deformation under load
(3) Extent of recovery from deformation.

Felting is influenced by—

pH and temperature of the milling liquor
Type of mechanical treatment
Duration of treatment.

As far as the actual fibres are concerned the following factors are to be taken into consideration—

Moisture content	Scaliness
Compressibility	Length
Porosity	Curl and twist
Ability to take a permanent set	Orientation in the material.

For practical purposes the felt industry can be divided into two main sections, one dealing with continuous or flat felts and the other with hoods.

I—Continuous (Flat) Felts

The bulk of continuous felts are made from wool noils or other fibres in the loose state, which are blended and carded to produce a loose web, which is then transformed into felt by *forming* followed by acid milling in stocks or on roller milling machines. They are also woven from yarn and then felted by milling under acid or alkaline conditions (e.g. for papermakers' felts).

Felts may be made from wool or a mixture of wool and hair such as cowhair, whilst cheaper felts contain varying proportions of cotton or other cellulosic materials. Casein fibres and other protein fibres may also be used in admixture with the foregoing.

Felts cover a wide range of uses, and include floor coverings, baizes, saddle cloths, lagging and insulating materials for industrial and domestic purposes, felt slippers, and "clothing" for drying cylinders.

The fastness requirements of dyed felts are usually not high, reasonably good fastness to light and water normally being the main essentials. Level-dyeing acid dyes are employed for wool and hair felts, and direct dyes or combinations of the

latter with neutral-dyeing acid dyes when cellulosic fibres are present.

Dyeing is carried out on the winch, and felts even up to 1 in. thick and weighing 8–10 lb./yd. can be penetrated. The use of suitable auxiliaries, such as Invadine NBN and Claysol WO, assists penetration.

Felts often contain vegetable impurities, which are removed by carbonisation with sulphuric acid. If this is carried out after dyeing, changes in hue may result unless suitable dyes are selected. For example, Kiton Fast Red 2BLE is faster to this treatment than Kiton Red G and similar products.

The dyeing of carbonised felts can give rise to difficulties as regards levelling and penetration owing to residual sulphuric acid, which may be of the order of 8–9%, and it is usual to begin dyeing with Glauber's salt and selected level-dyeing acid dyes. Recent work has shown that the number of sulpho groups present in acid dyes affects the results obtained on carbonised materials[3].

Alternatively, the carbonised material may be neutralised with ammonia or sodium acetate, but this is difficult to control in bulk. Neolan dyes, on the other hand, dye carbonised pieces without prior neutralisation and cover up carbonising faults readily. Our investigations have shown that all piece-dyeing Neolan dyes are equally suitable, irrespective of the number of sulpho groups present in the dye molecule.

Felt mats are often decorated by stencil printing with acid, direct, and other types of dyes.

Proofing against vermin can be carried out with such products as dinitro-α-naphthol or cuprammonium, and mothproofing with suitable proprietary compounds.

II—Hat Felts

Wool noils are used for felts of cheaper quality, and rabbit or hare fur for the better qualities. Mixtures of wool and fur are also used.

In the manufacture of wool felts, the scoured and carbonised noils are opened and carded, and the lap so formed is wound on a revolving cone to give a *form* which is *settled* by soaking in acidulated water and passing through fluted rollers and then *planked* (acid-milled) in stocks.

For fur felts, the fur has first to be *carrotted* to improve its felting properties. Usually a mixture of an oxidising agent, an acid hydrolysing agent and sometimes a metallic catalyst is used. Mercuric nitrate and nitric acid are commonly used in this country. Speakman has recommended hardening the fibres with mercuric acetate and then softening the tips of the fibres with mercuric nitrate, which is stated to result in more rapid felting. The mercuric carrott is prohibited in Germany on the score of danger of mercurial poisoning, and two mercury-free carrotts are made by Degussa A.-G. of Frankfort, both consisting of two solutions—

(1) AUROFELT—
  (a) Hydrogen peroxide, phosphoric acid, and sodium pyrophosphate
  (b) Ferric nitrate and nitric acid

(2) ARGYROFELT—
  (a) Hydrogen peroxide, phosphoric acid, and sodium pyrophosphate
  (b) Nitric acid, ferrous sulphate, and phosphoric acid

The latter mixture is stated to give a snow-white carrott[4]. There are numerous American patents on this subject.

The carrotted fur is opened, *blown* to remove impurities, blended, made into a *form* by drawing over a perforated cone, hardened, *settled*, and *planked* or *bumped* by milling with sulphuric acid.

DYEING

For mixture hats, the fur or wool is dyed in the loose condition in open pans or circulating machines using dyes fast to acid milling from the aggregated (Cloth Fast), Acid Alizarin, or chrome ranges. The last type of dye, however, is not universally applicable, as the chrome taken up by the fibre may interfere with subsequent felting operations.

Hoods are dyed in the partly or fully planked condition in the following types of machines—

(1) PADDLE— Acid dyes are employed, and there is always the danger of producing crease marks or "crow's feet" by this method of dyeing.

(2) ROTARY DRUM— This type of machine consists of a perforated drum divided into four compartments and rotating in a rectangular box which can be heated. Temperatures of 85–90°C. are generally not exceeded, and the dyeing of both wool and fur felt hoods is confined to level-dyeing acid dyes. Somewhat higher temperatures are obtainable, however, by enclosing the machine. Similar trouble with crease marks is encountered as with the paddle machine.

(3) CASSÉ AND OBERMAIER MACHINES consist of a circular container in which the dye liquor is agitated by a swirling motion, temperatures of about 95°C. being obtainable. Level dyeings are obtained, but there is the danger of crease marks.

(4) CONE— The hoods are placed over each other on a perforated cone, and the dye liquor is pumped from the outside through the cones. Temperatures approaching 95°C. are obtainable, and the pressure generated facilitates penetration. The advantage of cone dyeing is that the hoods are stationary and therefore their condition is preserved, but sometimes difficulties may be experienced in obtaining the same hue throughout a batch of hoods. Crease marks are not produced.

Owing to the higher temperatures possible in dyeing on cones and the Cassé type of machine, Neolan dyes can be used, which are of special interest for certain hues which cannot be dyed sufficiently fast to water with acid dyes. For example, a heavy nigger brown dyed with a combination of Tartrazine, Kiton Red G, and Alizarine Sapphire Blue CB is not as fast as a similar hue dyed with a combination of Neolan Yellow GR, Neolan Pink BA, and Neolan Blue 2G when subjected to a modified S.D.C. water test[5].

Hoods may also be dyed in the half-planked condition, which entails the use of dyes such as the Fullacines, which show reasonable fastness to acid milling.

It is generally accepted that fur felt requires more dye than wool felt, which may be attributed either to optical effects or to differences in affinity of the two materials. An investigation of the latter point was carried out as follows—

The acid content of white wool and grey fur felt was first estimated, giving 1·8% sulphuric acid in the wool felt and 2·4% sulphuric acid in the fur felt.

Dyeing was carried out on a thermostatically controlled oil-bath set at 130°C., which gave a gentle boil of the actual dye solutions. A liquor ratio of 50 : 1 was employed and was kept constant by the use of finger condensers[6]. A number of level-dyeing acid dyes normally employed in the hatting industry were dyed at two strengths, and in every case the amount of sulphuric acid used was 4%, which was obtained by an addition of 2·2% acid with the wool felt and 1·6% acid with the fur felt. Glauber's salt (40%) was used in addition, and dyeing carried out for a total period of 2 hr. at the boil.

The residual dye liquors were estimated absorptiometrically by means of an Ogal colorimeter*, and the amount of dye taken up by the fibre was obtained by difference. The results are given in the table, from which it will be observed that appreciably more dye is absorbed by wool felt than by fur felt under identical conditions, which to some extent accounts for the different amounts of dye required to produce similar shades on the two types of material. It will be noticed that differences are shown with individual dyes.

Felt		Depth (%)	Dye taken up by Felt (%) Kiton Fast Yellow 2G	Tartrazine	Kiton Red G	Kiton Red 6B	Alizarine Sapphire Blue CB
C.I. No.		—	639	640	31	57	1054
Wool	...	1·0	60	63	75	68	68
Fur	...	1·0	54	51	59	46	43
Wool	...	3·0	56	58	55	56	54
Fur	...	3·0	44	41	47	45	47

Two-coloured hats can be produced by dyeing with dischargeable acid or Neolan dyes, and treating one side of the hood with a hydrosulphite and a suitable thickener, followed by steaming. Colour discharge effects are also obtainable by incorporating selected dyes which withstand reduction. Special effects, such as "peach bloom" and "carded" finishes, are obtained by subjecting the dyed hoods to special finishing processes.

The following recent developments in the hatting industry can be mentioned—

(*a*) Production of so-called "conforming hats" in the U.S.A. These are made from wool and are crushable and adjustable to any shape[7]. Such finishes can be reproduced with the use of suitable emulsions of polyvinyl acetate.

(*b*) Other protein fibres, from casein, peanut, and soya-bean, may be used along with wool or fur, and the introduction of these materials in small amounts does not materially affect the dyeing properties of the hoods.

(*c*) A method has been put forward in America for the dyeing of hoods during planking on a multiroller machine, but is limited to standard shades[8].

(*d*) Optical bleaching agents are finding increasing application on hoods. They are colourless organic compounds having direct affinity for the fibre and possessing the property of absorbing light and re-emitting it in the form of a bluish or violet fluorescence. As a result whites are improved and pastel tones enhanced in brightness. Uvitex WS is of this type, and is applied with 4% acetic acid for 1 hr. at 50°C.[9]. In the case of dyed shades, treatment is carried out after dyeing. The treatment withstands finishing processes such as blocking.

I acknowledge my indebtedness to the Clayton Aniline Co. Ltd. for permission to give this paper.

* Ogal Duboscq-type colorimeter (Tintometer Co. Ltd.).

References

1 Freney, *Fibrous Proteins* (Bradford: the Society, 1946), pp. 178–192.
2 Martin, J.S.D.C., **60**, 325 (1944).
3 Townend and Simpson, *ibid.*, **62**, 47–52 (1946).
4 *BIOS*, 955: "German Hatters' Fur Industry".
5 The Society, *Second Report of the Fastness Tests Committee*, reprinted from J.S.D.C., **64**, 133-145 (April 1948).
6 The Society, *Report of the Committee appointed by Council to discuss the Dyeing Properties of Direct Cotton Dyes*, reprinted from J.S.D.C., **62**, 284 (Sept. 1946).
7 *Hatters' Gazette*, **72** (April 1948).
8 Tucker, *Amer. Dyestuff Rep.*, **37**, 483–493 (1948).
9 Landolt, *Textil-Rundschau*, **11**, 376–382 (1948).

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

The Editor,

SIR,

Mr. F. W. Thomas says that the woollen trade favours the use of the word *tenter* (J.S.D.C., **65**, 483 (Oct. 1949)). "Favours" is hardly the right word, for no other word is used for the machine in either the woollen or the worsted trade. The statement that the word "tenter" is used quite broadly for an operative who is working or tending any machine surprises me. I have never heard it used as such in any section of the trade or in any part of Britain, and despite numerous enquiries cannot find anyone who has. It is in one or two cases used as part of a definite compound name, e.g. *engine-tenter* or *back-tenter*.

Yours truly

C. O. CLARK

THE PRIORY

BOLTON

BRADFORD, YORKS.

31*st October* 1949

ERRATUM

Annual Reports on the Progress of Chemistry for 1948 (J.S.D.C., **65**, 542 (Nov. 1949)). The price should be given as 25s. 0d., not 15s. 0d.

Notes

Proceedings of the Council

At meetings of the Council, held at the offices of the Society, 32–34 Piccadilly, Bradford, on 19th October 1949 and 16th November 1949, the proceedings included the following items of interest—

SUMMER SCHOOL—It was resolved that the Summer School should be held during the week 16th–23rd September 1950, based on the Dyeing Department of Leeds University through the kind co-operation of Professor W. Bradley, and that it should be run in conjunction with the Extramural Department of the University. The Organising Committee would consist of the Chairmen and Honorary Secretaries of the West Riding and Huddersfield Sections of the Society (Mr. H. Foster, Mr. J. M. Goodall, Mr. D. Hanson, and Mr. H. Turner), Mr. C. L. Bird, and Mr. J. G. Evans, with Mr. J. Barritt (Honorary Secretary of the Society) as Chairman; Dr. R. L. Elliott and Dr. C. B. Stevens would act as Joint Honorary Secretaries to the Committee, the former to be responsible for social activities and visits, and the latter for the organisation of lectures and practical work.

FELTMAKERS' CO. MEDAL—The report of the Adjudication Committee for the Research Medal of the Worshipful Company of Feltmakers (see p. 8) was approved.

FASTNESS TESTS COMMITTEE—It was resolved to invite Messrs. J. V. Summersgill and E. Wilson to serve on this Committee.

DYERS' CO. MEDAL—The report of the Adjudication Committee for the Research Medal of the Worshipful Company of Dyers (see p. 8) was approved.

A.C.I.T. CONGRESS—Gratitude was expressed to Mr. E. A. Swift for his attendance at, and his report on, the twenty-second Annual Congress of the Association des Chimistes de l'Industrie Textile, which was held at Lyons on 16th–18th September 1949. The importance of the Congress had been shown by the attendance of members from several other European countries, and the 1950 Congress would be held at Lille, which was readily accessible from Great Britain.

MEMBERSHIP—Eighteen applications for ordinary and six for junior membership were approved.

Meetings of Council and Committees

November 1949

Council—16th
Finance—16th
Publications—15th
Colour Index Editorial Panel—30th
Wool Dyes—23rd
Fastness Tests—10th
Charter—16th
Society's Medal—16th

December 1949

Council—14th
Finance—14th
Publications—20th
Vat Dyes—7th
Summer School—1st and 15th

Front Cover of the *Journal*

Beginning with this issue, the *Journal* appears in a plain grey cover, on which is printed the list of contents. It is hoped that this new arrangement will be found convenient by readers.

Refereeing of Lectures

It has been decided by the Publications Committee, after consultation with the Honorary Secretaries of Local Sections, that the manuscripts of lectures for publication in the *Journal* shall be refereed in the same manner as are communications at present. It is felt that this will help to maintain the standard of the *Journal* in general, and will help to confirm that such papers are not to be regarded as in any way inferior to communications. This arrangement will apply to all papers submitted for consideration in 1950.

It should be emphasised that such refereeing will concern only manuscripts submitted for publication in the *Journal*, and that it is not intended in any way to censor the lectures which are to be given to local sections of the Society.

Classification of Abstracts

In this issue of the *Journal*, a new system of classifying abstracts, recently approved by the Publications Committee and indicated below, has been introduced.

I—Plant; Machinery; Buildings
II—Water and Effluents
III—Chemicals; Auxiliary Products; Finishing Materials
IV—Raw Materials; Intermediates; Colouring Matters
V—Paints; Enamels; Inks
VI—Fibres; Yarns; Fabrics
VII—Desizing; Scouring; Carbonising; Bleaching
VIII—Dyeing
IX—Printing
X—Sizing and Finishing
XI—Paper and other Cellulosic Products
XII—Leather; Furs; Other Protein Materials
XIII—Rubber; Resins; Plastics
XIV—Analysis; Testing; Apparatus
XV—Miscellaneous

Overseas Research Reports

The Technical Information and Documents Unit of the Board of Trade has begun to distribute, on a selective basis, a new type of summaries, bearing the reference ORR, which relate to reports made available to this country under a reciprocal arrangement with the Office of Technical Services, Department of Commerce, Washington, D.C. The reports deal mainly with research work carried out in U.S. Government, university, and other research establishments. In general, only one copy of each report is available and may be inspected at the T.I.D.U., 40 Cadogan Square, London S.W.1 (KENsington 5131, Extension 165), but photocopies may be bought on similar terms to those of ex-enemy reports.

Abbreviations and References

The abbreviations previously used in the *Journal* have been reviewed by a subcommittee of the Publications Committee, and the revised list, which does not differ greatly from the earlier list (J.S.D.C. **60**, 23 (Jan. 1944)), is given below. The method of citing literature references also has been modified, the date being indicated in parentheses after the page number.

Fair Copying

As a result of the Scientific Information Conference held in London during the summer of 1948, the Royal Society has subscribed to the fair copying declaration quoted below, and has invited other scientific and technical publishing societies to do likewise. The main purpose of the declaration is to improve the dissemination of information through libraries. The Council of this Society, after full discussion of the matter, has decided to follow the Royal Society by subscribing to the declaration for two years in the first instance.

Fair Copying Declaration

DECLARATION ON FAIR DEALING IN REGARD TO COPYING FROM SCIENTIFIC PERIODICALS

For some time scientists have discussed the problems, created by the Copyright Act, which arise when they wish to obtain reproductions of excerpts from scientific and technical periodical publications. In the normal course of their work, scientists occasionally require for frequent reference, copies of particular papers appearing in scientific periodicals which are not readily available to them. It is

Abbreviations and Symbols used in the *Journal of the Society of Dyers and Colourists* (January 1950)

No distinction is made in abbreviations between singular and plural

In special cases abbreviations and symbols other than those in the list may be used, but as far as possible they will be as given either in standard English dictionaries or in *British Standard* 813:1938

absolute	abs.	Fahrenheit	F.	*para-*	*p-*
acid value	A.V.	foot	ft.	parts per million	p.p.m.
alkyl radical (in chemical formula)	Alk	freezing point	f.p.	Patent	*P.*
alternating current	A.C.	French Patent	*F.P.*	potential difference	p.d.
ampere	amp.	gallon (Imperial)	gal.	pound	lb.
Angström unit	Å.	gallon (U.S.A.)	gal. (U.S.A.)	powder	pdr.
anhydrous	anhyd.	German Patent	*G.P.*	precipitate, -d	ppt.
approximate, -ly	approx., ca., ~	gram	g.	proportional to	∝
		greater than	>	*pseudo-* (organic compound)	*ψ-*
aqueous	aq.	halogen (in chemical formula)	Hal	qualitative(ly)	qual.
aryl radical (in chemical formula)	Ar	horse power	h.p.	quantitative(ly)	quant.
asymmetric (applied to organic compounds)	*as-*	hour	hr.	*racemic* (organic chemistry)	*r-*
atmosphere (pressure unit)	atm.	hundredweight	cwt.	recrystallised	recryst.
atomic	at.	hydrogen ion concentration (negative logarithm)	pH	refractive index	*n*
atomic weight	at. wt.			relative humidity	R.H.
		inch	in.	revolutions per minute	r.p.m.
Baumé	Bé.	inorganic	inorg.		
boiling point	b.p.	insoluble	insol.	saponification value	S.V.
British Patent	*B.P.*	iodine value	I.V.	saturate(d)	sat.*
British thermal unit	B.Th.U.			second	sec.
		kilogram	kg.	*secondary* (organic compound)	*sec.-*
calculated	calc.			soluble	sol.
Calorie (large)	kg.cal.	lævorotatory	*lævo*, (−) -	solution	soln.
calorie (small)	g.cal.	less than	<	specific	sp.
Centigrade	C.	logarithm (decadic)	log	specific gravity	sp. gr.
centimetre	cm.	logarithm (natural)	ln	square (in., cm., etc.)	sq.
compound	cpd.			substituted	subst.*
concentrated	conc.	maximum	max.	substitution on nitrogen, oxygen, etc.	*N-*, *O-*, etc.
concentration	concn.	melting point	m.p.	*symmetrical* (organic compound)	*s-*
configuration (carbohydrates and amino acids)	D-, L-	*meta-*	*m-*		
		metre	m.	temperature	temp.
constant	const.	microgram	μg.	*tertiary-* (organic compound)	*tert.-*
containing more than *n* carbon atoms	containing > *n* C	micron	μ.	turns per inch	t.p.in.
		milliampere	ma.	Twaddell	Tw.
corrected	corr.	milligram	mg.		
crystal, -line, -lised (adjective)	cryst.	millilitre	ml.	United States Patent	*U.S.P.*
cubic	cu.	millimetre	mm.	unsaturated	unsat.*
cubic centimetre	c.c.	millimicron	mμ. (10Å.)	unsubstituted	unsubst.*
decomposition	decomp.	millivolt	mv.		
density	*d*	minimum	min.	viscosity	*η*
derivative	deriv.	minute	min.	volt	v.
dextrorotatory	*dextro*, (+) -	molar (concentration)	M. or M-	volume	vol.
dilute	dil.	molecular, -e	mol.		
direct current	D.C.	molecular weight	mol. wt.	watt	w.
distil, -led	dist.	normal (concentration)	N. or N-	wavelength	λ
electromotive force	e.m.f.	*normal* (organic compound)	*n-*	weight	wt.
equimolecular	equimol.	normal temperature and pressure	N.T.P.	yard	yd.
equivalent	equiv.	organic	org.		
		ortho-	*o-*		
		ounce	oz.		

* Only in describing general formulæ in the Abstracts Section.

assumed that they take all reasonable steps to secure the original journals or separates of papers they require, either from the author or the publisher, but it is recognised that many requirements cannot be met from these sources. We have, therefore, agreed to make the following declaration to ensure that scientists have no undue difficulties in obtaining copies from libraries and other organisations supplying information. This declaration does not apply to books and other non-periodic or non-serial publications.

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OBITUARY NOTICE

Charles Frederick Brotherton

We regret to record the death, at the age of 67, of Charles Frederick Brotherton, a prominent figure in the chemical industry and a great philanthropist. The son of Charles Frederick Ratcliffe and his wife, sister of the late Lord Brotherton, who founded the chemical manufacturing firm of Brotherton & Co., Charles Brotherton joined the business in 1904 and succeeded to the chairmanship on the death, in 1930, of his uncle, whose name he afterwards took by deed poll.

At the end of the First World War, on the acquisition by the firm of the Mersey Chemical Works, Bromborough, he threw himself with characteristic energy into the task of building up a British hydrosulphites industry, and he also entered the dye-manufacturing field, specialising in particular in the metachrome range. In this, along with others, he played his part in building up the British dye and chemical industry to its present strength. Owing to failing health he retired from the chairmanship in February 1949, and was succeeded in that position by his younger brother, Capt. B. L. Ratcliffe, M.C.

His name is commemorated in Leeds by the Brotherton Wing of the Infirmary, the Charles Brotherton Chemical Engineering Laboratory, and the Brotherton Scholarships and Lectureships in Colour Chemistry and Chemical Engineering at Leeds University, all of which he endowed. He received the honorary degree of LL.D. from Leeds University in 1947. In 1939 he established the Charles Brotherton Trust by a gift of £250,000, the annual income from which is divided among the educational and medical charities of the six cities and towns with which the Brotherton chemical works are associated. G. BREARLEY

New Books and Publications

Fibre Science

Edited by J. M. Preston. Pp. xiv + 341. Manchester: The Textile Institute. 1949. Price, 30s. 0d.

Thirty years ago our knowledge of the constitution and structure of fibres was very meagre, being confined chiefly to wool, cotton, and silk. The rayons were merely on the threshold of their industrial life, while the idea of synthesising large fibre-forming molecules from small repeating units had not been conceived. Into that short span of time up to the present day has been packed a tremendous advance in fibre science on all fronts, which has culminated in the growth of a great synthetic fibre

industry, the full impact of which has yet to be felt.

In the face of such a rapid expansion, students and technologists alike have found it difficult to keep abreast of developments and, what is more serious, have thereby been prevented from applying the new principles to practical problems.

Recognising the need to bring these new advances to the knowledge of a wider range of people serving the textile industry, the Manchester College of Technology in conjunction with the Regional Advisory Council for Technical Education arranged a series of 18 lectures covering the constitution, structure, and properties of fibres and given by a group of scientists, many of whom have made original contributions in this field. With commendable foresight the Textile Institute has published these lectures in the present volume, which has been edited by Mr. J. M. Preston, who organised the original course.

Following an introduction outlining the scope of the work and a general account of macromolecular structure, chapters are devoted to the chemistry and structure of cellulose and its associated substances, the protein fibres, and synthetic fibre-forming polymers. X-Ray and optical techniques used to study the internal organisation of fibres are described, and an account is given of the determination of molecular weight and shape of high polymers in solution. The significance of the crystalline and amorphous regions in fibres and their influence on some physical and physicochemical properties is discussed. In the cellulosic field there is an interesting account of the organisation of the cell wall in plants in relation to the structure of fibres. The fine structure of fibres is considered in relation to dyeing and finishing.

On the whole the book presents a balanced account of the subject, based as it is on the efforts of thirteen contributors. However, some parts are not entirely above criticism, e.g. the chemical proofs of the structure of cellulose, amylose, chitin, and alginic acid are unnecessarily detailed, whilst in the chapter on swelling the discussion is confined almost entirely to cellulose.

The style and presentation are generally good, although the space allotted to certain structural formulæ, e.g. of Crystal Violet and Malachite Green (pp. 140 and 141), is excessive. Uniformity in size of units such as the benzene ring would have been desirable, whilst it is unfortunate that the style and abbreviations used by the Textile Institute for references in their Journal were not adopted throughout the book.

However, these are minor flaws in a book that can be recommended without hesitation to students and technologists. It is hoped that there will be further books of this calibre forthcoming.

P. W. Carlene

A Bibliography of Dyeing and Textile Printing

comprising a list of books from the sixteenth century to the present time (1946)

By L. G. Lawrie. Pp. 143. London: Chapman & Hall Ltd. 1949. Price, 15s. 0d.

This, the first work of its kind to be published for almost half a century, is not a bibliography in the bibliophile's sense of the word, but rather a check list of books on dyeing and printing published between 1500 and 1946. There is a main list of the books arranged alphabetically by author's name or by title where the author is unknown, a short-title list arranged in order of date of publication, and an index to the subjects of the books. Compilation of such a list could have been undertaken only as a labour of love, with the thrill of discovering a hitherto unknown title as the main if not the only reward for much tedious toil. This being so, it is with regret that it must be said that neither the collecting of the material nor its subsequent treatment has been well done. The list of books given is most incomplete and yet swollen. Incomplete because well over 100 omissions, some being well known books, have been noted, swollen because some "author's reprints", having no business in such a list, have been included. The author never seems to have made up his mind as to whether books on dyes should or should not go in: thus Perkin and Everest's book on natural organic dyes is included, but that of Mayer omitted. Sufficient care has not been bestowed on arranging the material. Thus, to cite two cases only, one book of le Normand's is placed under L, the other under N; an English edition of Alexis of Piemont is under A, and a German one under P. Another example of the mode of treatment is that accorded to Schultz's *Farbstofftabellen*, of which only the fifth edition is listed, without the slightest indication that in previous editions Schultz had P. Julius as co-author or that A. G. Green in 1894 published an English translation amplified by much material supplied by himself—yet on p. 11 the seventh edition is given as one of the author's sources of information! Added to such defects there are many printer's errors. Nevertheless, despite the serious shortcomings of this book, it can be of help to anyone whose interests urge them, whether for pleasure or profit, to delve into the history of the techniques of the dyeing and printing of textiles, for it is the only such list that has been published in this country.

C. O. Clark

Textile Laboratory Manual

By W. Garner. Pp. x + 478. London: The National Trade Press Ltd. 1949. Price, cloth 30s. 0d.

The manual comprises twenty-one chapters dealing with fibres, regain, strength, yarn and fibre properties, sizes, finishes, detection of metals, colour, dye testing, detergents, oils, water supplies, chemicals, biological and optical methods, viscosity, and statistical methods.

Whilst the compilation of technical data covering all aspects of a given subject is usually regarded as a task for a team of experts, Mr. Garner has undertaken this himself and has given us a treatise which covers most of the tests which a textile chemist is likely to encounter. In practice, of course, the reader will usually be interested in only a limited number of the tests, but with those he will wish to know the best available techniques. Such a compilation of data must therefore be of a uniformly high standard.

Prior to the details of each test or group of tests the author gives a short description of the subject matter itself. This treatment is necessarily inadequate for an understanding of the subject on account of limitations of space. The dual type of treatment moreover leads to passages such as: "Some of the effects of regain variation on textile testing may be given. All textile fibres swell in presence of water vapour; viscose, for example, is almost twice as thick when wet as when perfectly dry. This swelling has been made use of recently in the production of tightly woven cotton cloths, which are porous when dry . . . . The moisture content at saturation is wool— 33%, silk— 26%, cotton— 20%".

Selecting a few of the tests, on p. 6 the Pauly test is that originally given by Burgess and Rimington of the Wool Industries Research Association in 1929 (except that the present author states that sulphuric acid of sp. gr. 1·16 is used; this should be hydrochloric acid), whereas the reference he gives to Rimington in 1930 is to an improved form of the test, which should have been given. On p. 110, in the section on the measurement of regain, no mention is made of the Shirley Institute moisture meter. On p. 174 the author dismisses cursorily the test used by the recognised testing laboratories for the measurement of electrical insulation, but gives in great detail a test devised by himself. Again later, some five pages are devoted to a description of the Toussaint instrument for measuring colour, but only an inadequate outline of those instruments designed by physicists in accordance with accepted principles is given.

It is rather naïve to state of cotton that "one of the best qualities is Sakellarides". The Grex system of numbering counts is discussed, but as references as late as 1948 are given in the book, one might have expected to find that the proposals of the Textile Institute on this subject had been included. It is difficult to agree with the author when he states on p. 163 that the first wash given to wool fabrics causes only relaxation shrinkage.

In the matter of names, the work of the Society on the fastness of dyes to perspiration is attributed to Professor McSwiney only, whereas the actual work was carried out by Dr. Vass. On the other hand, one wonders why on pp. 182 and 190 the author includes with his data the words "Lister & Co. Ltd. Tech. Rep." In Fig. 7 in connection with the Kiton Red count the captions for the wet and dry chlorination are transposed.

The book is well produced and opens flat at any page. The type is pleasing and the photographs and diagrams are quite clear. P. W. CUNLIFFE

Textile Testing

By James Lomax. 2nd edition. Pp. viii + 221. London: Longmans Green & Co. 1949. Price, 21s. 0d.

It is twelve years since the first appearance of Mr. Lomax's book on Textile Testing. Since then, widespread research has added considerably to the techniques available. The Fastness Tests Committee of the Society and the Technical Committees of the Textile Institute have chosen agreed standard conditions for many of the more important tests. For the second edition of his book, Mr. Lomax has availed himself of this latter work as freely as delays in printing and the structure of an already established book would allow.

The book covers the elements of the subject, dealing clearly with essential principles. It is primarily a textbook for students rather than an exhaustive work of reference. None the less, the author is to be commended for his references to original papers, particularly in the section on chemical testing, whereby techniques may be learnt at first hand. The frequent use of addition sums in the text may be irritating to the more advanced, but it assists clear exposition. The treatment is systematic and balanced, and the scope comprehensive.

Some details of changes from the text of the first edition and certain omissions are worthy of note—

In his chapter on the identification of fibres, the author rightly lists staining tests as the least helpful, but the omission of any reference at all to Shirlastain A is an extravagance. It is also strange to find no mention at all of tests for moisture condition other than oven tests. Surely there is a field for electrical and other moisture meters in large sections of the industry? The section on the tensile testing of fibres, yarns, and fabrics has been brought up to date by the description of new instruments. Testing for the abrasion resistance and air permeability of fabrics has also received attention, though in this last instance it is unfortunate that the apparatus singled out for description should have been recently withdrawn from production.

The section on wool fibre measurement has been left much as before— the work of Daniels and Palmer on fibre sampling is not discussed. Mr. Lomax is patriotic enough to take even a micron count in fractions of an inch! A section on the measurement of yarn irregularity would also have met a present need. The most complete transformation is in the chapter on the statistical treatment of results— a very lucid, if necessarily short, account of significance tests, with the properties of the normal distribution slipped in undramatically.

The Second Report of the Society's Fastness Tests Committee, which appeared too late for its recommended methods to be included in the text, is discussed in an appendix together with proposed standard methods for other tests.

It will appear, therefore, that this is a well written, instructive manual in which sound, established practice exemplifies clear principles. It should be of great value to students.

W. J. ONIONS

Analytical Methods for a Textile Laboratory

Compiled by a committee of the American Association of Textile Chemists and Colorists. Pp. vii + 287. Lowell, Mass.: The Association. 1949. Price, $6·00.

This book is intended for the chemist in textile laboratories, and as it is obviously very useful and

may well be the forerunner of the textile chemist's perfect handbook, it merits as detailed consideration as space permits.

Simplicity and adaptability of method to average mill laboratory conditions have been achieved, but the advantages of methods using pH-meters, colorimeters, potentiometers, etc. should have been discussed. Standard methods are freely drawn upon, and British readers should note that parallel British Standard (occasionally Society of Public Analysts) methods exist, and should make use of these wherever possible. A good deal of compression could have been achieved, and there are a regrettably large number of mistakes. Many are obvious, but the most frequent and serious result from use of the fractional system of normality (e.g. "N/5" where 0·5N. is meant. Readers should beware on p. 115 *et seq.* and again on p. 143.

The book opens with eight pages of general instructions. The section on thermometers fails to mention immersion, and the advice on standardisation is not very sound. It is a pity that crystallising points are not used and a standard procedure is not described. Very sound chapters on reagents, standard solutions, and sampling follow. Then comes the strongest and most satisfactory section, rather more than half the book, devoted to analysis of chemicals, comprehensively and on the whole excellently done. Gums, oils, soaps, water, bleaching agents, phosphate mixtures are treated fully and soundly. For sulphated oils the A.S.T.M. procedure is given in detail and also Hart's "ammonia process" for combined sulphur trioxide. It is a pleasure to find that many very up-to-date methods are used. Inclusion of "average analysis" for each product is a very valuable feature. It is, however, important that this information should be accurate, and the writer notes two instances where this is not so (aniline and resorcinol).

The determination of finishing materials occupies about 25 pages, the second part being devoted to resins and resin finishes. The reviewer can think of a number of most useful tests that might have been included, prefers Skinkl's successive solvent extraction process for resin finishes, and is surprised at the omission of Barritt's pyridine method for acidity of wool. But this is a difficult subject, in which finality is yet far from being reached, and there is here gathered together most valuable material not readily available elsewhere.

Identification of dyes on the fibre, a difficult matter requiring expert knowledge and above all experience, is dealt with in under 20 pages. This is so out of date, faulty, and inadequate that it would have been better omitted altogether, and only the references given: clearly a section to be entirely rewritten when the first revision appears. Identification and determination of metals on textiles are scattered about various parts of the book, and only moderately well done. This subject is now so important that the book would do a great service if, in a future edition, it devoted a whole chapter to a comprehensive and sound treatment of the matter.

The book ends with an excellent chapter on the identification and determination of fibres, with several pages of beautiful photomicrographs. More tabulation would have been an improvement here, and the Textile Institute pamphlet should have been referred to.

A useful book, in spite of the many criticisms, which the writer hopes will be considered rather as suggestions, for it has great potentialities for future revisions and extensions. G. SPENCER

The Fibro Manual

A treatise on the characteristics and application of viscose rayon staple produced by Courtaulds, Limited

Edited by C. M. Whittaker. Pp. 311. London: Sylvan Press. 1949. Price, 21s. 0d.

An attempt has been made to cover the whole field of the processing of Fibro from spinning to finishing. Each section has been prepared by specialists, but there is none of the overlapping or discontinuity which often mars a work of this type. The production of Fibro is outlined only very briefly. The physical and chemical properties of the material are presented in readable form. The spinning section deals with tinting, the production of Greenfield top, and the spinning of Fibro by the cotton, woollen, worsted, flax, spun-silk, and jute systems. In a short section on fabric production great stress is laid on the individuality of Fibro. To those who have long recognised this fact its repetition becomes monotonous, but presumably there are still many who regard Fibro simply as a substitute for natural fibres. The section on preparing, dyeing, printing, and finishing, which occupies 145 pages out of a total of 300, is well detailed and contains many working recipes including a complete description of crease-resist finishing. There is justifiable emphasis on the testing, classification, and selection of dyes before use. Messrs. Courtaulds Ltd. were, of course, pioneers in this type of work, which has since and rather ironically been extended to investigations of the behaviour of dyes on natural fibres.

The hope is expressed that the reader will peruse the whole of the subject matter and so obtain an overall picture of Fibro processing. The book is admirably suited to this purpose; it contains much authentic and accurate information, and can be recommended as a useful addition to the textile literature. F. ASHWORTH

Textieltechnologie
Deel I— Chemische-technologie

By J. Lanczer. Pp. 528. Enschede, Holland: Stichting de Tex. 1949. Price, fl. 25.00 (approx. 50s. 0d.).

There are no illustrations in this Dutch book, and the machinery described in the text is to be dealt with in Part II, under the title *Mechanische Technologie*.

The author, a chemist–colourist and teacher of textile technology at the Enschede Textile High School, states quite fairly in the Foreword that the book has been written by a practical man, and is intended for those who are already engaged in the

trade, and also for those who are at the beginning of a colourist's career.

This has given the author an almost unrestricted latitude in the choice and treatment of material to be presented, and whilst much useful practical information is given for all, this is interspersed with portions suitable for beginners, such as (p. 194): "The printer . . . must above all be on the *qui-vive* for printing faults".

The scope of the book is very wide, and it has a natural resemblance in many ways to a collection of some of the well catalogued application manuals supplied by dyemakers. In one aspect, however, it does not follow this pattern, in that lists of products with particular reference to fastness properties are given in terms of the dyes which will *not* withstand a certain reagent. This method in many cases makes for a great saving in space, but the negative approach used leaves the reader to assume the properties of products not specifically mentioned by name.

The text is methodically laid out in clear-cut chapters (32 in all), which range from an Introduction by Professor R. Haller, and a short historical review of processing by L. A. Driessen (this achieves the abnormal by referring to the development of synthetic dyes without a mention of Perkin), to water purification, bleaching, mercerising, dyeing, printing, and finishing; casein, nylon, and acetate rayon are given separate chapters, whilst wool is dealt with under two chapters, firstly, pretreatment including dyeing and printing, and secondly finishing. Pp. 437–490 fall under the general heading of *The Laboratory*, giving useful general notes and the usual tables on the more common chemicals used by the colourist.

An errata list is supplied with the book consisting of over 100 mainly minor corrections, but in spite of this obviously careful clerical scrutiny an air of unreality to the true Yorkshireman is introduced on p. 59, where in a list of dye and auxiliary-product factories we are told that the name "Holliday" implies "Read Holliday & Sons Ltd., in Huddersfield (U.S.A.)"! This is a relatively harmless error, but does give substance to the query whether a book of this kind can hope to compete with better equipped organisations in supplying fully checked and reliable catalogues of dye names and detailed information, or with such bodies as the Society (via the *Colour Index*) in the provision of information on analogous dyes. The pitfalls of this latter work are exposed typically on p. 106, where a still uncorrected error quotes Caledon Golden Orange GS (ICI) as analogous to Indanthren Gold Orange 3G (IG). By bitter experience the student could learn the different effects of these dyes on cellulose by exposure of the fabric to light. Scrupulous accuracy is the only excuse for the existence of catalogues of dye names.

The book under review nevertheless has a wealth of practical recipes, and it will no doubt be of real value to the Dutch student colourist.

E. MARNEY

"AnalaR" Standards for Laboratory Chemicals

Formulated and issued jointly by The British Drug Houses Ltd. and Hopkin & Williams Ltd. Fourth, revised and enlarged edition. Pp. xviii + 302. London. 1949.

The fourth edition of this volume, now so well known to all chemists, contains specifications for 58 compounds which were not included in the third edition. For the most part these have been chosen with two definite objectives— (i) to introduce at least one compound of each of the more common elements (compounds of beryllium, caesium, cerium, lithium, selenium, strontium, tellurium, thallium, thorium, and titanium are now included), and (ii) to introduce a liberal selection of organic analytical reagents. The latter include both those used in inorganic analysis, e.g. sodiumdiethyldithiocarbamate and diphenyldithiocarbazone (dithizone), and those used for the identification of organic compounds by the formation of derivatives of definite melting-point, e.g. 3:5-dinitrobenzoyl chloride, 2:4-dinitrophenylhydrazine.

All the earlier specifications have been revised in the light both of progress in analytical chemistry and of experience of users' requirements. Specific solubility tests and assays have been included for a large number of chemicals. New analytical methods employed include (1) electrolytic deposition techniques both for the assay of certain metallic salts and for the removal of the principal metal in order that alkali and alkaline-earth impurities can be determined, thereby avoiding unsatisfactory precipitation methods; (2) the use of the polarograph for determining certain metallic impurities; (3) the Karl Fischer technique for determining the moisture content of organic liquids.

Greater precision of analytical methods has inevitably shown that some of the maximum impurity limits previously quoted were underestimated. In some instances the figure has been retained by improving the quality of the chemical, but where this has not been possible and a higher limit is quoted, it is emphasised that the material now supplied is at least equal in purity to that issued under the old standards.

F. F. ELSWORTH

A Chemistry of Plastics and High Polymers

By P. D. Ritchie. Pp. viii + 288. London: Cleaver-Hume Press Ltd. 1949. Price, 25s. 0d.

Many university students who intend entering industry after graduation must find, when they consider the plastics industry, that they have only the vaguest ideas on the chemistry of high polymers. In the quest for more knowledge on the subject, they find that, although there are many excellent monographs and textbooks, these are often too highly specialised, and so they fail to obtain a general picture of the subject. It is to such persons that Dr. Ritchie's book should particularly appeal, although others concerned with the use of polymeric materials will find that it contains much valuable information.

As the needs of the organic chemist have been kept primarily in view, the structural and synthetic aspects of the subject are kept well to the fore, although the physical treatment has not been neglected.

It has been the author's aim to demonstrate the astonishing breadth of the field, and he has not given the well known industrial plastics preference over the natural polymers, such as the terpenes and silicates.

Naturally, when such has been the author's intention, it is impossible, in a book of this size, to give anything approaching a complete review of the individual classes of polymer. By omitting theories of historical interest, and many controversial subjects, the important modern concepts have been reviewed, the treatment being thoroughly up-to-date. Unfortunately, limitations of space have necessitated the omission of full literature references, but extensive suggestions for further reading have been included. W. S. SHORT

FIAT Review of German Science 1939-1946
Physics of Liquids and Gases

Senior author E. Kappler. Pp. viii + 348. Office of Military Government for Germany: Field Information Agencies Technical. 1948. No price. [In German.]

This review of German scientific literature is divided into four parts, devoted respectively to the physics of liquids (177 pages), the physics of gases (81 pp.), fluctuation phenomena (6 pp.), and colloid physics (64 pp.). Each part is further divided and subdivided in a manner which facilitates reference to works dealing with a particular topic.

The first part includes sections dealing with the structure of liquids, molecular association in liquids and solutions, thermodynamics and statistical mechanics of liquids and solutions, surface and interfacial tension, diffusion, viscosity, thermal conductivity, the propagation of sound in liquids, dielectric, optical, and magnetic properties, and the electrical conductivity of liquids.

The part on the physics of gases is similarly divided into sections on thermodynamics and kinetic theory, transport phenomena, the conduction of sound through gases, dielectric and optical properties, and finally a long section on electrical conductivity and the various kinds of discharge through gases.

The brief review of fluctuation phenomena includes work on Brownian motion and on the limiting sensitivity of measuring instruments.

The final section, on the physics of colloids, reviews briefly investigations concerning various aspects of each of the main types of colloidal system except emulsions, viz. aerosols, sols, gels, dispersed powders, sintered structures, capillary systems, and foams. The subsequent sections deal with particle size and shape, separation and aggregation, surface phenomena, the structure of high polymers and their mechanical and thermal properties, optical and electrical properties, and the viscosity of colloids.

This FIAT review provides a comprehensive abstract of German scientific literature published during the war years rather than a critical survey of the state of each subject. For this reason it is unlikely to appeal to the general reader, but those especially interested in the physical chemistry of dyeing will find much that has an indirect bearing on the subject, particularly in the sections on the physics of liquids and colloids. Very little of the work reviewed is directly concerned with textile technology. D. A. CROOKS

New Books Received

Indian Institute of Science 1938–1948. Bangalore: Bangalore Press. [1949] Pp. xii + 139.

Power Laundry Directory Year Book 1948. London: The Trader Publishing Co. [1949] Pp. 308. 15s. 0d.

The "Textile Recorder" Book of the Year, 1948–1949. Manchester and London: Harlequin Press Co. Ltd. 1949. Pp. 224. 21s. 0d.

Colours and How We See Them. H. HARTRIDGE. London: G. Bell & Sons Ltd. 1949. Pp. xi + 158. 15s. 0d.

The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents. Vol. I. *Chemical Analysis.* M. B. JACOBS. New York and London: Interscience Publishers. 2nd enlarged edition. 1949. Pp. xviii + 788. 96s. 0d.

Basic Physics: Vol. 3, part IV— *Sound*; Part V— *Light.* S. L. MARTIN and A. K. CONNOR. Melbourne, Australia: Whitcombe and Tombs Pty. Ltd.

A New Dictionary of Chemistry. S. and L. MACKENZIE MIALL. London, New York, and Toronto: Longmans, Green & Co. 2nd edition. 1949. Pp. ix + 589. 60s. 0d.

Practical Warp Gaiting. W. MIDDLEBROOK. Stockport: Cloister Press Ltd. 1948. Pp. iv + 107. 3s. 6d.

Textiles for Salesmen. E. OSTICK. London: Sir Isaac Pitman & Sons Ltd. 5th edition. 1948. Pp. xii + 207. 10s. 6d.

Fluorescence and Phosphorescence. P. PRINGSHEIM. New York and London: Interscience Publishers. 1949. Pp. xvi + 794. 120s. 0d.

Aromatic Diazo-compounds and their Technical Applications. K. H. SAUNDERS. London: Edward Arnold & Co. 2nd edition. 1949. Pp. xi + 442. 50s. 0d.

Textile Testing— Physical, Chemical, and Microscopical. J. H. SKINKLE. Brooklyn, N.Y.: Chemical Publishing Co. Inc. 1949. Pp. xii + 953. $7·75.

Plastics Technological Dictionary. A. M. WITTFORT. Munich: Carl Hanser Verlag. 1948. Pp. 310.

Reports on German Industry

I.G. Farbenindustrie A.-G., Ludwigshafen
Emulsions and Dispersions— Wax–Zirconium Oxychloride Water-repellent Finishes— Testing of Detergents for White Goods

FDX 624* (PB 70,488; Microfilm M145).

A microfilm of a number of reports, in German, including a 22 pp. report written in 1938 on dispersing agents, protective colloids, colloid mills, etc. Another report written in 1938 deals with the production of wax–zirconium oxychloride emulsions as water-repellent finishes for textiles, and another written in 1936–37 with the laboratory testing of detergents for white goods. C. O. C.

Anorgana G.m.b.H., Gendorf— I.G. Farbenindustrie A.-G., Hoechst
Dyes— Wetting, Anti-crease, Finishing, Waterproofing, and other Textile Agents— Detergents— Betaine Derivatives

FDX 621* (PB 70,343; Microfilm C14).

A microfilm copy, in German, of papers read at joint meetings of Anorgana and I.G., Hoechst staff in 1937 and

* Material available for inspection at Board of Trade, German Division, Technical Information and Documents Unit, 40 Cadogan Square, London, S.W.1.

1938 and at meetings of the I.G.'s Textile Auxiliary Agents Committee. There are over fifty papers dealing with work on acid, direct, vat, and solubilised vat dyes, and a copy of the agreement about Indigosols made between Durand & Huguenin, I.C.I., and I.G. In addition there is a large number of papers dealing with textile auxiliary agents, the crease-resisting and hydrophobing of viscose rayon, waterproofing, etc. C. O. C.

Titangesellschaft, m.b.H., Leverkusen
Titanium Dioxide

FD 1414/49*.

Copies of 8 patent applications dealing with the manufacture of titanium dioxide, one dealing with the cleaning of non-white substances, e.g. natural and synthetic rubbers, plastics, paper, linoleum, artificial fibres, etc. by means of rutile titanium dioxide, and one on the effect of titanium dioxide in the production of copper ruby glass. C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen
Determination of Cotton and Rayon Staple in Fabrics— Relation between Detergent Properties and Molecular Structure— Magnesia— Igepons etc.

FDX 623* (PB 82,073; Microfilm X48).

A microfilm of various reports, in German, among them being the following— a simple method for determining the proportions of cotton or rayon staple in fabrics; relation between detergent properties and molecular structure, in which it is shown that change of temperature may reverse the order of efficiency of two detergents; description of a laboratory washing machine for evaluating detergents; examination of soot with an electron microscope; photometric determination of the amount of cellulose or other doubly refracting fibres in a liquid; a new process for extracting magnesium oxide from dolomite; and the preparation of Igepons in a single phase from the corresponding fatty acids and sodium isethionate. C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen
Mild Washing Process for Linen

FD 1596/49* (PB 17,690).

A report, in German, of 23 pp. After an alkaline pretreatment the goods are treated with soap solution at pH 8–9, and cleansing is completed by adding a synthetic detergent to the soap solution. The preliminary scouring with soap alone renders inorganic soil much more readily removable by synthetic detergents. C. O. C.

I.G. Farbenindustrie A.-G., Chemische Werke Hüls, Marl, Recklinghausen
I.G. Standard Methods of Analysis

FDX 572* (PB 73,860; Microfilm N26).

A microfilm of two lists giving, in German, the chemical and trade or works names of about 600 compounds, together with the number of the I.G. standard analytical method to be applied to each. Fifty of these methods are described. C. O. C.

I.G. Farbenindustrie A.-G., Chemische Werke Hüls, Marl, Recklinghausen
299 I.G. Methods of Analysis

FDX 573* (PB 74,800; Microfilm N27).

A microfilm, in German, of 299 methods of analysis for various inorganic and organic compounds, adopted as standard by the I.G. C. O. C.

* Material available for inspection at Board of Trade, German Division, Technical Information and Documents Unit, 40 Cadogan Square, London, S.W.1.

Abstracts from British and Foreign Journals and Patents

(The Titles of Patents are abridged and modified)

Abbreviations

BrC British Celanese Ltd. **CAC** Clayton Aniline Co. Ltd. **Ciba** Ciba Ltd. **CN** Compagnie Nationale de Matières Colorantes et de Produits Chimiques du Nord Réunies Etablissements Kuhlmann. **DH** Durand & Huguenin A.-G. **DuP** E.I. du Pont de Nemours & Co. **Gy** J. R. Geigy A.-G. **ICI** Imperial Chemical Industries Ltd. **IG** I.G. Farbenindustrie A.-G. **LBH** L. B. Holliday & Co. Ltd. **S** Sandoz A.-G. **YDC** Yorkshire Dyeware & Chemical Co. Ltd.

The above abbreviations are used after the names of commercial dyes. The following abbreviations are used in the titles of abstracts of patent specifications— **Kuhlmann** Compagnie Nationale de Matières Colorantes et de Produits Chimiques du Nord Réunies Etablissements Kuhlmann. **Du Pont** E. I. du Pont de Nemours & Co. **I.C.I. Ltd.** Imperial Chemical Industries Ltd. **Sandoz** Sandoz A.-G.

I— PLANT; MACHINERY; BUILDINGS

Payen Enclosed Piece-dyeing Machine. Anon. *Teintex*, **13**, 286–289 (Aug. 1948).

The principles underlying this new, patented enclosed piece-dyeing machine are described and illustrated. It is claimed (*a*) that the bath volume remains constant throughout the dyeing period, (*b*) that the operative temperature of the bath is maintained at 100°C. in contrast to 95°C. in the case of other machines, and (*c*) that the machine effects a steam saving of about 35%. R. B. W.

Symposium on Pilot Plant Design and Construction. American Chemical Society. *Ind. Eng. Chem.*, **40**, 2011–2053 (Nov. 1948).

The papers relate chiefly to chemical engineering research facilities and processes at various laboratories in U.S.A. Polymerisation units for thermosetting resins and the production of methacrylamide and acrylonitrile by catalysis are dealt with in separate papers. G. L.

PATENTS

Maintaining Constant Tension while Winding a Web. Oilgear Co. *B.P.* 626,034.

Impregnating and Drying Fabric under Controlled Tension. R. P. Allen and Seiberling Rubber Co. *U.S.P.* 2,472,057.

The fabric is passed through an impregnating liquor and then by means of a tension-controlling device to a drier. This tension control consists of means for rotation, in passing around which the fabric is looped in such a way as at least to tend to move the control with respect to the impregnating bath and the drier as the fabric tends to shrink as a result of the impregnation. A stalled torque motor is connected with a reversible switch and with the tension control so that it can supplement or oppose movement of the tension control with respect to the impregnating bath and the drier. C. O. C.

Horizontal Drum Washing Machines. J. W. Chamberlin and J. F. Horvath. *B.P.* 626,720.

A washing machine comprises a base frame, a rotatable drum, movable support means attached thereto, a second movable support means, and resilient connections between the supports and between the second set of supports and the base frame. This enables the machine to be run at both tumbling and extraction speeds while maintaining dynamic balance, and so avoids transmission of undue vibration to the base frame. C. O. C.

Liquor-control System for Laundry Washing Machines. Dole Valve Co. *B.P.* 627,593.

A control system for the temperature and level of the washing liquor, particularly applicable to non-automatic or semi-automatic laundry washing machines, comprises dual automatic temperature control mixing valves, a liquor delivery duct, two supply valves for controlling flow of liquor from the mixing valves to the delivery duct, manual control for the supply valves, and two members

responsive to the liquor level for shutting the supply valves. C. O. C.

Garment-finishing Apparatus. G. W. Johnson. *B.P.* 625,875.

A preheating device for supplying dry steam, air, or both to the inside of a porous shape over which the garment is distended comprises a double-walled dished member having an open-top central cavity within its inner wall, and an annular dish-shaped closed chamber between its inner and outer walls. Steam is circulated through the closed chamber, maintaining the walls in a heated condition, and is afterwards discharged into the central cavity, and thence in a dry state to the inside of the garment form. G. E. K.

Sleeve Press. Prosperity Co. Inc. *B.P.* 624,749.

A machine for pressing tubular articles such as shirt sleeves has co-operating pressing elements of V cross-section. The lower pressing element, on which the tubular article is sleeved, fits within the upper element. The V formation of the lower element is expansible outwardly to effect the pressing operation. A maximum area of the article is pressed in one operation, and then, if desired, the entire area can be pressed in one more lay. L. C.

Stocking-drying Machine. W. M. Cissell. *B.P.* 624,833.

A machine for drying socks and stockings has a number of hollow forms mounted vertically upon a circular revolving platform rotated by hand. Hot air provided by a fan and heater within the base is directed through the hollow forms to dry the socks or stockings. The forms are tilted forward to an inclined position to facilitate unloading and reloading. L. C.

Removing Non-inflammable Liquid from Materials. United Wallpaper Inc. *B.P.* 627,234.

Apparatus for removing moisture or non-inflammable liquids rapidly and safely, avoiding scorching, from wallpaper or cloth, comprises a first section in which open flames from rotatable burners with vertical adjustment are in direct association with the material to be dried for a predetermined period to heat the liquid for subsequent evaporation in a second section. The first part of the latter receives the hot gases from the first section, and the second part subjects the material to heated air from a heating chamber associated with the burners in the first section. A conveyor belt is used to transport the material through both sections. S. V. S.

II—WATER AND EFFLUENTS

Recent Water-softening Techniques. J. Borgé. *Teintex*, **13**, 358–363 (Sept. 1948).

A review, with corresponding plant diagrams, of the chalk, gyrator, and ion-exchange processes of water-softening. R. B. W.

Control of Washing-off Waters. J. Raux. *Teintex*, **14**, 149–153 (April 1949).

The importance of correct control of the conductivity of washing-off liquors in various branches of the textile industry is stressed. An apparatus is described for the measurement of conductivity and is based on the Wheatstone bridge principle. B. K.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Experiments on the Photolysis of Aqueous Solutions of Chlorine, Hypochlorous Acid, and Sodium Hypochlorite. K. W. Young and A. J. Allmand. *Canadian J. Res.*, **27B**, 318–331 (April 1949).

The photodecompositions of aqueous solutions of chlorine, hypochlorous acid, and sodium hypochlorite have been studied under a wide variety of conditions. Particular attention has been paid to the quantum efficiency of the reactions involved, and to the proportions of the products formed. Reaction mechanisms are suggested to account for the results obtained. A. S. F.

Zirconium as a Fixative for Dyes. W. B. Blumenthal. *Rayon Synthetic Text.*, **29**, 87–89 (Oct. 1948).

An outline of the chemistry of zirconium is given with particular reference to its high affinity for oxygen, the readiness with which it forms co-ordination compounds, and its amphoteric nature. Its textile applications in the production of water-repellent finishes and its use in pigment finishes are described. H. K.

Investigations into the Production of Rongalite. II—Rate and Mechanism of the Decomposition of Rongalite Solutions. T. I. Kunin. *J. Appl. Chem.* (*U.S.S.R.*), **22**, 199–206 (Feb. 1949).

Stability of Rongalite. T. I. Kunin. *Tekstil. Prom.*, **9**, 27–30 (Feb. 1949).

A further study has been made of the decomposition of Rongalite solutions using the analytical technique described in the first paper of the series (J.S.D.C., **65**, 246 (May 1949)). The reaction rates found under various conditions are characterised by second-order equations. The rate of the initial dissociation into sulphoxylate and formaldehyde is proportional to the pH of the solution. The formaldehyde decomposes at a rate proportional to the concentration of water. Below 80°C. decomposition of formaldehyde proceeds at a greater rate than the decomposition of sulphoxylate; there is a reduction in pH as reaction proceeds. Above 100°C. sulphoxylate has the higher rate of decomposition and the pH rises. The reaction is complicated by the evolution of volatile products. Detailed reaction schemes are given for the various conditions, the overall equations being as follows—

Below 80°C.—

$$6NaHSO_2,CH_2O + 3H_2O = 4NaHSO_3 + 2H{\cdot}COONa + 2H_2S + H{\cdot}COOH + 3CH_3OH$$

About 100°C.—

$$3NaHSO_2,CH_2O = 2NaHSO_3,CH_2O + CH_2S + NaOH$$

About 120°C.—

$$6NaHSO_2,CH_2O = 2Na_2SO_3 + Na_2S + 6CH_2O + 2SO_2 + H_2S + 2H_2O$$

In presence of strong acids—

$$2NaHSO_2,CH_2O + H_2SO_4 = Na_2SO_4 + 2CH_2O + 2H_2O + SO_2 + S$$

A. E. S.

Application of Non-ionic Compounds in the Textile Industry. J. P. Sisley. *Teintex*, **14**, 53–73 (Feb. 1949).

Non-ionic compounds which are employed in the textile industry are discussed under the following groupings—softening agents, wool-scouring agents, emulsifying agents for removal of mineral oil from wool, products for acid milling of wool, levelling agents in dyeing, stripping agents, levelling agents for naphthols. A tabulated list of Continental and American non-ionic auxiliary products is given, classified according to chemical grouping, together with an indication of usage. B. K.

Use of Alkarylsulphonates in the Textile Industry. M. J. Vallée. *Teintex*, **13**, 399–409 (Nov. 1948).

A comprehensive review is given of the variety, classification, preparation, and uses of the alkarylsulphonates in the textile industry. These compounds are formed by the condensation of long-chain aliphatic compounds with benzene, naphthalene, or other condensed nuclear hydrocarbon or derivative. Tables are given of the polymeric aliphatic hydrocarbons obtained from propylene, butylene, and *iso*butylene, and also of the possible isomers of benzene with three propylene radicals. H. H. H.

Relation between Chemical Structure and Performance [of Surface-active Agents]. W. D. Scott and D. S. P. Roebuck. *Chem. and Ind.*, 627–631 (2nd Oct. 1948).

The mechanism of detergency is analysed in the light of recent research. The function of the various hydrophilic groups in detergent molecules is discussed. Data illustrating the effects of structural variation in the hydrophobic part of the molecule on wetting power are presented. Breakdown of surface–soil adhesion and redeposition are briefly surveyed. G. L.

Organised Structure in Soap Solutions. G. S. Hartley. *Nature*, **163**, 767–768 (14th May 1949).

The author's simple picture of the aggregates in clear mobile solutions of paraffin-chain salts, as essentially liquid in nature and spherical in form, is discussed in conjunction with a lamellar micelle picture which had been suggested by X-ray diffraction data. The difficulties of the latter view are that in order to account for all the water, the lamellæ must be assumed to be separated laterally by a greater depth of water than that held

between the ionic faces, and also that when oil is dissolved in the soap micelles, the increase of long spacing is much greater than is directly accounted for by the additional volume inside the micelle. Reasons are given for believing the micelles to be of closely constant size in any one solution and to vary but little with the concentration, and calculated data for potassium laurate and sodium tetradecyl sulphate are consistent with the spherical hypothesis. H. H. H.

Wetting Agents and Auxiliary Products. J. B. Speakman. *Chem. and Ind.*, 456–460 (17th July 1948).

The chemistry of auxiliary products has been surveyed in the widest possible sense with emphasis on the special importance of monomers, new cross-linking agents, and inorganic compounds for modifying fibre and fabric properties. An attempt is made to classify auxiliary products in accordance with their ability to modify either the surface or the internal structure of the fibres to which they are applied. The need for new types of auxiliary products is indicated. G. L.

α-Monostearin and Sodium Stearate as Emulsifying Agents. H. H. G. Jellinek and H. A. Anson. *J.S.C.I.*, **68**, 108–114 (April 1949).

The areas occupied by α-monostearin and sodium stearate at the interface have been calculated from the interfacial tensions at 70°c. for the systems— (1) water-white oil containing α-monostearin against water, (2) water-white oil against water containing sodium stearate, and (3) water-white oil with α-monostearin against water containing sodium stearate. Separation phases at 70°c. for these systems have been studied. The phase volume ratio was kept at 1 : 1 in all experiments. α-Monostearin gives water-in-oil emulsions, but the addition of sodium stearate causes inversion to oil-in-water emulsions. The amount of the latter required to bring about the inversion is very nearly independent of the concentration of the α-monostearin. The emulsion stability is increased by a combination of the two agents. W. J. M.

Surface-active Agents in Aqueous and Non-aqueous Media. H. Lomas. *J.S.C.I.*, **68**, 37–40 (Feb. 1949).

The nature of dispersing agents and their effect on the properties of the solid–liquid interface are discussed. A brief description of the effect of salt on the system and an outline of the nature of the forces acting between dispersed particles is given. W. J. M.

Sodium Silicates in the Textile Industry. R. C. Merrill. *Amer. Dyestuff Rep.*, **38**, 428–435 (30th May 1949).

Sodium silicate is available in a wide range of alkalinities and provides the textile industry with a cheap and efficient agent for detergency, buffering, peroxide-stabilising, and coating. It also has useful adhesive and colloidal properties. The scope of its use is described with respect to kier boiling and scouring, bleaching, weighting, sizings and coatings, dyeing and printing, and fireproofing. Special uses are suggested such as the preshrinking of wool and the formation of a protective lining in kiers and pipes conveying peroxide. W. J. M.

Investigation on Cellulose Reactions. VI— Note on the Formation of Carboxymethyl and Sulphoethyl Celluloses. T. Timell. *Svensk Papperstidning*, **52**, 61–63 (15th Feb. 1949).

It has been shown that the number of glycol groups in different carboxymethyl celluloses, determined by means of periodate oxidation, can vary considerably according to the previous history of the ether. The relatively high proportion of such groups in the majority of the preparations investigated shows, however, that the primary hydroxyl is apparently the first to react. The glycol analysis was also carried out on a series of nine different sulphoethyl celluloses prepared under the same conditions. Initially, only the primary hydroxyl reacts, and the number of glycol groups drops linearly with increasing degrees of substitution. The ratio between the number of reacted primary and secondary hydroxyls falls during the course of the reaction. A comparison between the different methyl, ethyl, carboxymethyl, and sulphoethyl celluloses so far investigated shows good agreement in this respect. S. V. S.

Germicides for Army Mobile Laundries. T. H. Vaughn, A. L. Sotier, E. F. Hill, J. E. Simpson, and W. M. Lee. *Ind. Eng. Chem.*, **40**, 2054–2059 (Nov. 1948).

Work leading to the adoption of a chlorine-liberating germicide, sodium benzenesulphonchloramide (Monochloramine B), for use in army and navy washing operations is described. Studies showed that this agent produced marked reduction of bacterial count. Its use in cases of emergency in commercial laundries, which normally rarely need a germicide, is suggested. G. L.

PATENTS

Wetting Agent. H. G. Figdor and E. F. Houghton & Co. *U.S.P.* 2,471,945.

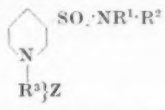
A mixture of a water-soluble surface-active agent of the anionic, cationic, or non-ionic type and a diester of a polyethylene glycol of general formula—

$$R^1{\cdot}CO{\cdot}O{\cdot}(CH_2{\cdot}CH_2{\cdot}O)_n{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}R^2$$

(n = 5–22; R^1 and R^2 = unsubstituted, saturated alkyl groups, containing straight or branched chains, the sum of the carbon atoms in R^1 and R^2 being 12–16 and the difference between them < 5), e.g. a mixture of sodium dodecyl sulphate (40 parts) and the esterification product (60) of 1 mol. of hexaethylene glycol with 2 mol. of caprylic acid, readily disperses in water and has very high wetting and penetrating properties. C. O. C.

3-Alkylsulphamylpyridinium Salts— Wetting and Detergent Agents having Germicidal Properties. M. F. Zienty and Upjohn Co. *U.S.P.* 2,473,121.

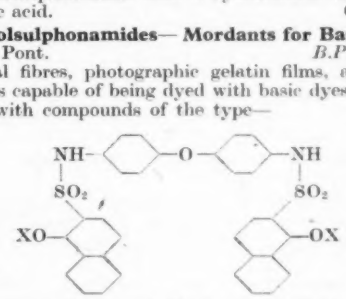
Compounds of general formula—



(R^1 = an alkyl radical of 8–16 C; R^2 = H or an alkyl radical of 8–16 C; R^3 = a lower alkyl, lower alkenyl, or aralkyl radical; Z = halogen or an alkyl sulphate radical) are readily prepared by warming a mixture of an N'-alkyl-3-pyridinesulphonamide with a hydrocarbon ester of an inorganic acid. C. O. C.

Naphtholsulphonamides— Mordants for Basic Dyes. Du Pont. *B.P.* 620,803.

Animal fibres, photographic gelatin films, and other materials capable of being dyed with basic dyes are mordanted with compounds of the type—



(X = H or an acyl or carbalkoxy group containing 2–5 C atoms) to give increased fastness to light and washing. Compounds in which the diphenyl ether link is replaced by the residue of other aromatic diamines, e.g. 1:5-diaminonaphthalene, benzidine, or 4:4′-diaminostilbene, are also used. R. K. F.

Impregnating Composition. British Thomson-Houston Co. Ltd. *B.P.* 620,697.

A composition which confers moisture-, abrasion-, and flame-resistance and is suitable for impregnating permeable electric-cable insulation comprises a mixture of a modified polyester with a synthetic wax prepared from a chlorophthalic anhydride and an amine, e.g. amylamine. E. C.

Phosphonyl and Thiophosphonyl Chlorides— Flameproofing Agents, Textile Finishing Agents, Plasticisers, etc. W. H. Woodstock and Victor Chemical Works. *U.S.P.* 2,471,472.

An addition product of phosphorus pentachloride and a mono-olefin of general formula $R^2R^1C{:}CH_2$ (R^1 and R^2 = one of the following pairs— alkyl and alkyl, alkyl and aryl, aryl and aryl, aryl and hydrogen, or aryl and chlorine) is heated with phosphorus pentoxide or pentasulphide in an inert solvent, and the solvent and

by-product phosphorus chloride compounds formed are separated from the unsaturated phosphorus compound. The alkenylphosphonate esters formed, e.g. 1-styrylphosphorus oxydichloride, are valuable as plasticisers, textile treating agents, etc. The chloroalkylphosphonate esters produced, e.g. dibutyl 1-chloroamyl-2-phosphonate, are useful as flameproofing agents for textiles, fire-retarding plasticisers, etc. C. O. C.

Starch oxidised with Nitrogen Dioxide. W. O. Kenyon, C. C. Unruh, and Eastman Kodak Co. *U.S.P.* 2,472,590.

Water-insoluble oxidised starch is obtained by treating starch with nitrogen dioxide (e.g. dissolved in a halogenated hydrocarbon) long enough to impart a carboxyl content of not $< 12\%$, washing the product with water, and drying. The product is useful as a textile size for improving the adherence of basic dyes. The heavy-metal salts obtained from it are useful as mordants for textiles. Used as a finish on surgical gauze it prevents its adherence to body tissues. C. O. C.

Stabilised Dry Rosin Size. J. C. Barthel, A. R. Davis, E. N. Poor, and American Cyanamid Co. *U.S.P.* 2,471,714.

Dry rosin size is stabilised against oxidation by incorporation of 0·25–0·5% of its weight of phenothiazine. C. O. C.

Halogen-containing Insecticides. Geigy Co. Ltd., J. E. Balaban, and F. Manchester. *B.P.* 627,549.

Insecticidal compositions comprise a compound of general formula $R{\cdot}CHCl{\cdot}CX_3$ (R = a subst. or unsubst. benzene ring, X = Cl or Br), together with a solid, semi-solid, or liquid diluent; e.g. pumicestone, charcoal, or kieselguhr is steeped in a solution of α-phenyl-$\alpha\beta\beta\beta$-tetrachloroethane (10 parts by weight) in benzene (20), and dried under reduced pressure. The product is useful as a moth repellent. J. W. B.

Siloxane Resins for Varnishing Cloth, Impregnating Glass-fibre Fabrics, etc. Dow Corning Corpn., W. R. Collings, H. N. Fenn, and H. J. Fletcher. *B.P.* 626,909.

Resins which can be cured by heating for a short time at 250°C. are obtained from mixtures containing phenyl- and methyl-substituted silicon chlorides produced by treating silicon tetrachloride with phenyl and methyl Grignaud reagents by first evaporating off the remaining silicon tetrachloride and the low-boiling methyl-substituted silicon chlorides. The residue is mixed with methylsilicon trichloride. The mixture is then hydrolysed, and the products are copolymerised to yield a bodied resin. C. O. C.

Applications of Acrylic and Vinyl Pastes. J. A. Hetherington. (XIII, p. 92.)

Formaldehyde–Thiol Condensates — Vulcanisation Accelerators and Agents for Improving the Adhesion of Rubber to Textiles. M. W. Harman and Monsanto Chemical Co. (XIII, p. 93.)

Amino Resins. British Resin Products, L. R. Anthony, E. M. Evans, and R. W. H. Wicking. (XIII, p. 93.)

Aqueous Emulsions of Mixed Phthalic Glyceride and Melamine–Formaldehyde Resins. D. W. Light and American Cyanamid Co. (XIII, p. 93.)

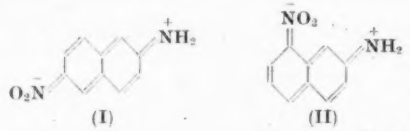
Amino-Aliphatic Guanamines — Intermediates for Resins for treating Textiles. J. T. Thurston and American Cyanamid Co. (XIII, p. 93.)

β-Thiocarbamylthiocarboxylic Acid Derivatives — Fungicides, Vulcanisation Accelerators and Activators. B. F. Goodrich Co. (XIII, p. 93.)

IV— RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Separation of 6- and 8-Nitro-2-naphthylamine. H. H. Hodgson and J. Ratcliffe. *J.C.S.*, 1040 (April 1949).

6- and 8-Nitro-2-naphthylamines can resonate into the quinonoid structures I and II, of which I is by far the more stable and makes a greater contribution to its resonance hybrid. In consequence, the 8-nitro will be more basic than the 6-nitro isomeride, and a separation is now reported from their mixture which depends on this property, viz. the prior solubility of the 8-nitro-2-naphthylamine in very dilute hydrochloric acid (1 c.c. of acid (sp. gr. 1·18) per 100 c.c. of water); this appears to be more complete and much less tedious than the fractional crystallisation processes of previous workers (cf. Veselý and Jakes, *Bull. Soc. chim.*, **33**, 942 (1923); Saunders and Hamilton, *J. Amer. Chem. Soc.*, **52**, 638 (1932)).



(I) (II)

H. H. H.

A Convenient Preparation of 8-Nitro-1-naphthylamine. H. H. Hodgson and J. Ratcliffe. *J.C.S.*, 1314–1315 (May 1949).

The best method extant, from the standpoint of yield, for the preparation of 8-nitro-1-naphthylamine is that of Hodgson and Crook (*J.C.S.*, 1844 (1936); cf. *B.P.* 439,632), which, however, requires the use of ammonia at 130°C. under pressure for the hydrolysis of the mixture of 4-, 5-, and 8-nitrophthalo-1-naphthylimides obtained when phthalo-α-naphthalide is nitrated, the amines being subsequently separated by preferential solubilities in 10% aqueous sulphuric acid. An alternative hydrolysis of this mixture by boiling ethanolic hydrazine hydrate at atmospheric pressure is now described, which dispenses with an autoclave, and, by working at a lower temperature, minimises the tar formation to which *peri*-derivatives of naphthalene are prone. From the results, it would appear that the 8-nitrophthalo-1-naphthalide is preferentially hydrolysed. Since phthalylhydrazide can be extracted by ammonia from the residues, it follows that only the naphthalene portion of phthalo-α-naphthylimide is nitrated. H. H. H.

Chloro Derivatives of 2-Nitrodiphenylamine. V. F. Borodkin. *J. Appl. Chem.* (*U.S.S.R.*), **21**, 987–994 (Oct. 1948).

In a study of the formation of mono- and dichloro-2-nitrodiphenylamines from aniline, or a chloroaniline, and a dichloronitrobenzene, it is shown that isomers of the last may be placed in the following order of reactivity—2:5 > 2:3 > 2:4 > 2:6. The reactivity of the amino group in the isomeric chloroanilines is in the order—$p > o > m$. A. E. S.

Reactions of Aromatic Nitro-compounds with Alkaline Sulphides. II— The Three Dinitrobenzenes. H. H. Hodgson and E. R. Ward. *J.C.S.*, 1316 (May 1949).

o-Dinitrobenzene reacts with sodium hydrogen sulphide in aqueous methanol to give sodium *o*-nitrothiophenoxide, 2-2′-dinitrodiphenyl sulphide by subsequent reaction between this product and *o*-dinitrobenzene, and 2:2′-dinitrodiphenyl disulphide, formed probably by oxidation of the above thiophenoxide by the concurrently liberated sodium nitrite. The many previous failures reported in the literature to obtain 100% yield of *m*-nitroaniline by reduction of *m*-dinitrobenzene with alkaline sulphides would appear to be due to concurrent formation of *m*-phenylenediamine, and its subsequent interaction with the sodium thiosulphate always present in alkaline sulphide reductions (cf. Bernthsen's thiosulphate process for Methylene Blue). Sodium hydrogen sulphide in hot methanol is now found to give 90–95% yields of *m*-nitroaniline free from azoxy compound even under ice-cold conditions, whereas *p*-dinitrobenzene reacts to give mainly 4:4′-dinitroazobenzene with some 4:4′-diaminoazobenzene, *p*-nitroaniline, and probably *p*-phenylenediamine. H. H. H.

Reactions of Aromatic Nitro-compounds with Alkaline Sulphides. III— Dinitronaphthalenes. H. H. Hodgson and E. R. Ward. *J.C.S.*, 1187–1190 (May 1949).

A dinitronaphthalene reacts with alkali sulphides, and, in particular, with sodium hydrogen sulphide, to form, mainly, a monoamine by reduction, and a sodium mercaptide by replacement of a nitro with a sodium thio (–SNa) group, the ratio of these products varying according to the electropositivity of the carbon atom to which the

reactive nitro group is attached. 1:2- or 1:8-Dinitronaphthalene gives only thiol, whereas the 1:3-, 1:5-, 1:6-, and 2:7-isomers give mainly the amine. 1:4-Dinitronaphthalene behaves like the 1:2-isomer, except that approx. 4% of monoamine is also formed. The results are in accord with Hodgson's theory of sulphide reduction (J.S.D.C., **59**, 246 (1943); cf. Hodgson and Turner, *J.C.S.*, 318 (1943)), and with the previous conclusions of the present authors. H. H. H.

Separation of 1:5- and 1:8-Dinitronaphthalenes. B. P. Fedorov and A. A. Spryskov. *J. Appl. Chem. (U.S.S.R.)*, **21**, 1014–1018 (Oct. 1948).

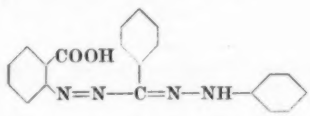
Determinations were made of the solubility of 1:5- and 1:8-dinitronaphthalene in aniline, sulphuric acid, acetone, and methanol at various temperatures. Methods were evolved for the separation of these isomers from technical dinitronaphthalene by means of fractional crystallisation from sulphuric acid or aniline. A. E. S.

Suggested Identification of *cis*-Azobenzene with an Equimolecular Mixture of Hydrazobenzene and Azoxybenzene. R. J. W. le Fèvre and P. Souter. *J.C.S.*, 1595–1597 (June 1949).

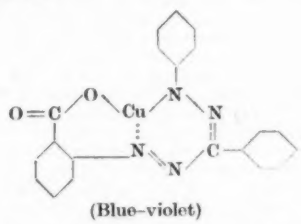
The mixture named in the title has been examined at 25°c. in benzene solution, and differs from *cis*-azobenzene in two respects, viz. (*a*) polarity measurements lead to an apparent moment of about 1·6 D. (in contrast to 3·0 D. for *cis*-azobenzene); and (*b*) illumination (daylight) causes only a very slight increase of dielectric constant (in contrast to the marked decrease already recorded for *cis*-azobenzene). Hydrazobenzene and azoxybenzene do not appear to interact under the conditions stated, and the apparent moment for their mixture is of the order to be expected from that of each solute separately. H. H. H.

Formazyl Complexes— I. R. Wizinger and V. Biro. *Helv. Chim. Acta*, **32**, 901–912 (May 1949).

Formazyl compounds having a carboxyl or hydroxyl group *ortho* to the formazan chain, e.g.—



afford very fast complexes with metals, those with copper and nickel possessing very intense colours. The metal is simultaneously linked in two *ortho*-condensed subsidiary valency rings, e.g.—



(Blue–violet)

Complexes derived from formazyl-2:2′-dicarboxylic acid are remarkably acid-stable. Replacement of the *meso*-phenyl by the NC– group produces a hypsochromic effect. H. H. H.

4-*m*-Nitrobenzeneazo-1-naphthol— Discrepancies in the Literature. J. van Alphen and G. Drost. *Rec. Trav. chim.*, **68**, 54–56 (Jan. 1949).

The coupling product of *α*-naphthol and the by-product of the coupling of *α*-naphthyl ethyl ether, both with diazotised *m*-nitroaniline, are identically 4-*m*-nitrobenzeneazo-1-naphthol of m.p. 241–243°c. (decomp.), as stated by Shingu (*Sci. Papers Inst. Phys. Chem. Research* (Tokio), **35**, 78, 119 (1938)). The observation by Meyer *et al.* (*Ber.*, **47**, 1741, 1743, 1749 (1914)) of its formation is correct, as also their suggestion that it must be formed at the moment of the coupling, since the azo-ether is quite stable towards both boiling acetic acid and caustic soda, but their m.p. of 288°c. (decomp.) is incorrect. H. H. H.

The Fundamental Fallacy of the Free Radical Hypothesis as Applied to the Decompositions of Aromatic Diazo-Compounds. H. H. Hodgson. *Chem. and Ind.*, 653–654 (9th Oct. 1948).

Criticisms of the free-radical hypothesis in interpreting the decompositions of diazo compounds are summarised. The proponents of the free-radical theory suggest that the C–N bond in $\geqslant$C–N=N–X ruptures first, but it is pointed out that the X–N=N• radical so formed would have extremely high explosive potentialities. Furthermore, Hodgson and Marsden (*J.C.S.*, 208 (1940)) by reaction of the stabilised *p*-nitrobenzenediazonium ion with nitrobenzene obtained a good yield of *pp′*-dinitrodiphenyl, under the most unfavourable conditions for the free-radical hypothesis. A. S. F.

***cis*-Diazocyanides.** H. H. Hodgson. *Chem. and Ind.*, 428–429 (3rd July 1948).

This letter is in reply to one by Waters (*ibid.*, p. 301 (1948)) in support of the evidence put forward by Le Fèvre *et al.* (*ibid.*, p. 158 (1948)) for the existence of *cis*-diazocyanides. The main criticism of the present author rests on the claim that the *cis*- to *trans*-diazocyanide change is photochemically reversible, which was based on the results of a series of experiments with silver nitrate and an *anti*-diazocyanide in alcoholic solution. By analogy, it would be expected that if a solution of an *anti*-diazocyanide in alcohol containing *β*-naphthol were exposed to light, the photochemical production of *syn*(*cis*)-diazocyanide would produce an arylazo-*β*-naphthol in excellent yield. This reaction was found by Hodgson not to occur to the slightest extent in the case of *p*-nitrobenzene-*anti*-diazocyanide, and he concludes that an adequate background of chemical evidence does *not* exist in support of the *cis*-diazocyanide formula, and that the structural isomerism of these compounds remains unrefuted. A. S. F.

***cis*-Diazocyanides.** R. J. W. Le Fèvre and J. Northcott. *Chem. and Ind.*, 543 (21st Aug. 1948).

In reply to the letter of Hodgson (*ibid.*, p. 428) criticising the chemical evidence for the existence of *cis*-diazocyanides, additional evidence on the photochemical *cis–trans* change has now been obtained. It is suggested that Hodgson failed to detect the formation of *p*-nitroazobenzene-*β*-naphthol when an alcoholic solution of *p*-nitrobenzene-*anti*-diazocyanide containing *β*-naphthol was irradiated, owing to the strong absorption of near ultraviolet radiation by the *β*-naphthol. If only the *anti*-diazocyanide is irradiated, however, and the *β*-naphthol added after, a dark red precipitate is obtained. The criticism by Hodgson of Waters' experiments with silver nitrate–*anti*-diazocyanide mixtures (*ibid.*, p. 301) is therefore described as irrelevant. A. S. F.

Isomeric Aryldiazocyanides. R. J. W. Le Fèvre, J. Northcott, and I. R. Wilson. *Chem. and Ind.*, 732–733 (13th Nov. 1948).

This letter is in reply to Hodgson (*ibid.*, p. 270), who asserts that the experimental work described in Le Fèvre's original communication on this subject refers either to mixtures of *cis*- and *trans*-forms, or to *trans*-forms only. The interpretation of the spectral evidence proposed by Hodgson is challenged, and evidence is given which shows that the experimental material used in Le Fèvre's initial experiments was in the same state before and after testing. A. S. F.

Effects of Solvents and Structure on the Thermal Transformation of *cis*- into *trans*-Diazocyanides. R. J. W. Le Fèvre and J. Northcott. *J.C.S.*, 944–951 (April 1949).

The rates of thermal *cis–trans* interconversion of ten-diazocyanides in one solvent (benzene), and of *p*-chlorobenzenediazo cyanide in eight different solvents, have been compared. The reactions show first-order kinetics with frequency factors between 10^{12} and 10^{15} per sec., and energies of activation of 21–26 kg. cal./mole. The lower *A* and *E* values apply in the case of non-polar solvents, changing to the higher as the polarity of the solvent increases. No regular correlation of either *k* or *E* with solvent properties could be discerned. For various diazocyanides in benzene, the influence of the substituents is expressed by—

$$E = E_0 + 2{\cdot}9\boldsymbol{R}T(\mu + 0{\cdot}209\,\mu^2)$$

where E_0 is the energy of activation of benzenediazocyanide, and μ is the dipole moment of the appropriate C_6H_5X compound. H. H. H.

Replacement of the Diazonium by the Azido Group in Acid Solution. H. H. Hodgson and W. H. H. Norris. *J.C.S.*, 762–763 (March 1949).

A rapid method is described for obtaining steam-volatile aryl azides in excellent yields (> 70% of *m*-nitrophenyl azide from *m*-nitroaniline) from aryldiazonium sulphates by reaction with hydroxylamine sulphate in sulphuric–acetic acid medium. β-Azidonaphthalene, stated by Forster and Fierz (*J.C.S.*, 91, 1942 (1907)) to have been successfully prepared by them only by the direct action of diazotised β-naphthylamine on hydrazoic acid, was also isolated. Examples given are azides from *o*- and *p*-nitroaniline, *p*-chloroaniline, *p*-nitro-*o*-toluidine, *o*- and *m*-nitro-*p*-toluidine, α-naphthylamine, and *m*- and *p*-phenylenediamine. H. H. H.

Configurations of α- and β-Naphthalenediazocyanides. R. J. W. Le Fèvre and J. Northcott. *J.C.S.*, 333–337 (Feb. 1949).

The dipole moments of the four known forms corresponding to the formula $C_{10}H_7{\cdot}N{:}N{\cdot}CN$ are claimed to be explicable for *cis* and *trans* forms of the α- and β-naphthalenediazocyanides respectively. The phenyl and *p*-tolyl analogues, which are homogeneous oils at ordinary temperature, have properties which indicate that the *trans* configurations largely predominate. H. H. H.

Replacement of the Diazonium by the Cyano-group in Neutral Solution. H. H. Hodgson and F. Heyworth. *J.C.S.*, 1131–1133 (May 1949).

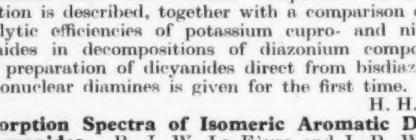
The preparation of cyanides and dicyanides from diazonium and bisdiazonium compounds in neutral solution is described, together with a comparison of the catalytic efficiencies of potassium cupro- and nickelocyanides in decompositions of diazonium compounds. The preparation of dicyanides direct from bisdiazotised homonuclear diamines is given for the first time. H. H. H.

Absorption Spectra of Isomeric Aromatic Diazocyanides. R. J. W. Le Fèvre and I. R. Wilson. *J. C. S.*, 1106–1107 (May 1949).

Five pairs of isomeric diazocyanides have been examined in ethereal solution between 220 and 600 mμ. Differences between related forms are not great and lie more in ε_{max} than in λ_{max}. The data are claimed to be compatible with the geometrical explanation proposed originally by Hantzsch for these compounds. H. H. H.

Thermal Decomposition of *o*-Hydroxydiazonium Compounds. J. de Jonge, R. Dijkstra, and P. B. Braun. *Rec. Trav. chim.*, **68**, 430–432 (June 1949).

Although the thermal as well as the photo-decomposition of diazonium compounds in water generally leads to the corresponding phenol, the photodecomposition of *o*-hydroxydiazonium compounds of benzene or naphthalene is peculiar in that the benzene nucleus carrying the diazonium group is converted into a 5-membered ring with generation of a carboxyl group—



Experimental evidence is now submitted that the thermal decomposition of the above compounds in dilute solution may be identical with the photodecomposition. Reference is made also to Vaugham and Phillips (*J.C.S.*, 1560 (1947)), whose data on the thermal decomposition of some nitrobenzenediazo-oxides in the solid phase at 50–80°c. may be interpreted as a partial decarboxylation of a nitro*cyclo*pentadienecarboxylic acid. H. H. H.

Photodecomposition Products of some Diazonium Salts. J. de Jonge and R. Dijkstra. *Rec. Trav. chim.*, **68**, 426–429 (June 1949).

Secondary reactions are largely avoided by irradiation of a very dilute solution of a diazonium salt at a temperature slightly above 0°c., and by using a high light intensity from a Philips water-cooled super-high-pressure mercury lamp SP 500. In this way 85–90% yields of the corresponding phenols were obtained from *p*-dimethylaminobenzenediazonium borofluoride, 2-methoxybenzenediazonium-5-sulphonic acid, and *p*-hydroxybenzenediazonium sulphate. From *p*-naphthaquinone diazide in aqueous solution, however, only 15% of 1:4-dihydroxynaphthalene, and from 2:6-dibromoquinone 1:4-diazide in an acidified solution (pH ~ 1) only 30% of 2:6-dibromoquinol could be isolated. H. H. H.

Replacement of the Diazonium by the Nitro-group. V— New Preparations of 2:3- and 2:5-Dinitrotoluene from Monoamines and the Simultaneous Introduction of Two Nitro-groups into some Homonuclear Diamines. H. H. Hodgson and F. Heyworth. *J.C.S.*, 1624–1625 (June 1949).

2:3- and 2:5-Dinitrotoluene are more readily prepared by neutralising the solutions of the diazonium sulphates from 3- and 5-nitro-*o*-toluidine with calcium carbonate and subsequently decomposing them with cupro-cupric sulphite in the presence of excess sodium nitrite than by previously described methods. The route from 5-nitro-*o*-toluidine was preferred to that from 6-nitro-*m*-toluidine. The same procedure permits the preparation of the dinitro compounds from bisdiazotised *m*- and *p*-phenylene- and *m*- and *p*-tolylene-diamines. There appears to be no previous literature reference to the simultaneous replacement of two diazo by two nitro groups in the same aromatic nucleus. H. H. H.

Influence of the Concentration of Sulphuric Acid on the Hydrolysis of 2-Naphthol-8-sulphonic Acid. I. I. Vorontsov. *J. Appl. Chem.* (*U.S.S.R.*), **21**, 1002–1005 (Oct. 1948).

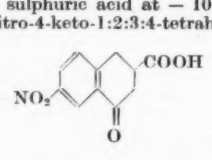
2-Naphthol was sulphonated to yield a mixture of its 6- and 8-monosulphonic acids. After the addition of a further quantity of sulphuric acid the sulphonation mixture was divided into portions, to which various amounts of water were added. Further reaction proceeded at 90°c. In presence of water the 2:8-isomer was hydrolysed at a rate which reached a maximum when the proportions of water and acid were equimolecular. In absence of water the main product was 2-naphthol-6:8-disulphonic acid, resulting from the further sulphonation of both monosulphonic acids. On the basis of these results sulphonation conditions for the production of 2-naphthol-6-sulphonic acid and 2-naphthol-6:8-disulphonic acid have been worked out. A. E. S.

Derivatives of ββ′-Diphenyladipic Acids. H. E. Fierz-David, L. Blangey, and M. Uhlig. *Helv. Chim. Acta*, **32**, 1414–1433 (Aug. 1949).

The nitration and relatively less ready halogenation of the diphenyladipic acids afford *pp′*-disubstituted acids; other isomers can be isolated only in small amounts; these *pp′*-acids serve for the preparation of acid wool dyes. Attempts to sulphonate these diphenyladipic acids led by water scission to the corresponding diketohexahydrochrysenes. The dihydrodiphenylmuconic acids may be obtained from the dimethyl *aa′*-dibromodiphenyladipates, and their *cis–trans* isomerism established by rearrangement. Azo dyes from the *trans-pp′*-diaminodihydrodiphenylmuconic acids exhibit only small differences from the saturated dyes from *pp′*-diaminodiphenyladipic acid. From these diamines may be produced compounds of chrysene structure by water fission, ring formation being retarded by *p*-halogeno and *p*-nitro groups. The ditertiary glycols prepared from the diphenyladipic esters by Grignard reactions split off water with consequent ring formation only if the tertiary carbon atoms are substituted by alkyl groups; substitution by phenyl groups causes the fission of water in the aliphatic chain. A hydroxy-*o*-chrysenequinone can be prepared from diketohexahydrochrysene by bromination, fission of hydrobromic acid, and subsequent air oxidation. H. H. H.

Aminohydroxynaphthoic Acids. I— Synthesis of 6-Amino-4-hydroxy-2-naphthoic Acid ("Carboxy γ-Acid"). W. F. Beech and N. Legg. *J.C.S.*, 1887–1889 (July 1949).

Nitration of 4-keto-1:2:3:4-tetrahydro-2-naphthoic acid in concentrated sulphuric acid at − 10 to − 5°c. yields principally 6-nitro-4-keto-1:2:3:4-tetrahydro-2-naphthoic acid—



which is converted by bromination, dehydrobromination, and subsequent reduction of the nitro group to 6-amino-4-hydroxy-2-naphthoic acid, the carboxylic analogue of γ-acid. H. H. H.

New Intermediates and Dyes. I— 4-*tert.*-Butylphthalic Acid and its Anhydride. R. B. Contractor and A. T. Peters. *J.C.S.*, 1314 (May 1949).

4-*tert.*-Butylphthalic acid and its anhydride have been prepared in 35% yield as follows— 4-*tert.*-Butyl-*o*-xylene (I) was prepared from *o*-xylene, *tert.*-butyl chloride, and zinc chloride. Oxidation of I by boiling aqueous potassium permanganate gave 4-*tert.*-butylphthalic acid, readily converted into its anhydride (II) by boiling with acetic anhydride. Condensation of II with benzene in the Friedel–Crafts reaction afforded (probably) 2-benzoyl-5-*tert.*-butylbenzoic acid, which was readily cyclised by 20% oleum into β-*tert.*-butylanthraquinone. H. H. H.

Carbazoletrisulphonic Acid. V. F. Borodkin and T. V. Malkova. *J. Appl. Chem.* (*U.S.S.R.*), **21**, 849–853 (Aug. 1948).

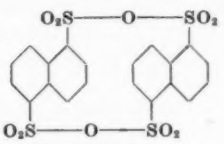
The sulphonation of carbazole by various methods to the trisulphonic acid leads in each case to the 1:3:6-isomer. Alkali fusion of this gives 1-hydroxycarbazole-3:6-disulphonic acid, which on treatment with weak sulphuric acid at 170–175°c. yields 1-hydroxycarbazole. A. E. S.

Photoconductivity of Naphthalene and Anthracene. N. S. Bayliss and J. C. Riviere. *Nature*, **163**, 765 (14th May 1949).

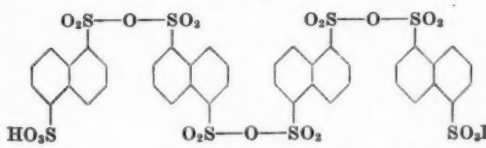
Both naphthalene and anthracene, when melted and allowed to solidify between two platinum electrodes approx. 0·5 mm. apart, show weak photoconductivity when exposed *in vacuo* to the unfiltered radiation from a quartz mercury-vapour lamp. With applied voltages of 50–360, the photocurrents are detectable with a good galvanometer and are of the order 10^{-8} amp., superposed on a rather variable dark current. As in the case of dyes, the photocurrents are quenched if air is admitted to the system. By using calibrated wire screens to reduce the incident light intensity, the currents are directly proportional to the intensity, and the relation between current and voltage is exponential. The photocurrents are quenched if a fused silica cell containing distilled water is interposed in the path of the light, suggesting that the active radiation is $\lambda = 1849$A. of the mercury spectrum. H. H. H.

An Anhydride of Naphthalene-1:5-disulphonic acid. L. Blangey and H. E. Fierz-David. *Helv. Chim. Acta*, **32**, 631–634 (May 1949).

Naphthalene-1:5-disulphonic acid is converted by 20% oleum at temperatures below 50°c. into an anhydride, which on treatment with ammonia readily gives a mixture of naphthalene-1:5-disulphonamide and 1-sulphamylnaphthalene-5-sulphonic acid. The same anhydride arises during the preparation of naphthalene-1:5-disulphonic acid by the sulphonation of naphthalene with 66% oleum. No decision could be arrived at between the possible structures—



and



H. H. H.

Reactions of Benzoyl Peroxide. D. H. Hey. *J. R. Inst. Chem.*, 256–257 (Oct. 1948).

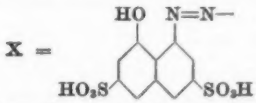
The reactions between the peroxides and aromatic compounds give rise to homolytic aromatic substitution, as do certain diazo compounds, and the normal direct influences of substituent groups are not observed. These reactions frequently provide convenient routes for the synthesis of unsymmetrically substituted diaryl derivatives in good yield. Among the less straightforward reactions of this type is that prepared from the half (1)-ester of 4-nitrophthalic acid, which in reactions with benzene gives rise to a mixture of 4- and 5-nitrodiphenyl-2-carboxylic acids, indicating two isomeric peroxides to have been formed. The action of thionyl chloride on the half esters of an unsymmetrical dibasic acid results in a mixture of acid chlorides, and this type of rearrangement must be involved in the preparation of the above peroxides. Phthalic acid peroxide is much more stable than benzoyl peroxide, and does not react readily with boiling benzene; but with nitrobenzene at 140°c. reaction takes place readily to give a mixture of 2- and 4-nitrodiphenyl-2′-carboxylic acids. On the other hand, phenylacetyl peroxide is much less stable, and in benzene solution it gives dibenzyl by dimerisation. The close similarity between the reactions of those peroxides and those of various diazo compounds is illustrated, and for the decomposition of a covalent diazo compound the author prefers the mechanism—

$$Ar—N=N—X \rightarrow Ar + X—N=N$$
$$X—N=N \rightarrow N_2 + X$$

rather than one based on the decomposition of the diazonium ion. The use of peroxides as sources of free radicals has provided a satisfactory explanation of the so-called "peroxide effect", and has opened up new methods for atomic chlorination (using sulphuryl chloride) and homolytic carboxylation (using oxalyl chloride). H. H. H.

Azo Dyes from 5-Amino-1-naphthol and its Derivatives. VI— Potentiometric Titration of Azo Dyes and some Conclusions about their Fine Structure. B. A. Poray-Koshits and L. S. Efros. *J. Gen. Chem.* (*U.S.S.R.*), **18**, 929–935 (1948): *Chem. Abs.*, **43**, 4467–4469 (1949).

Glass-electrode titrations of 8-X-5-amino-1-naphthol (I), 4-X-5-amino-1-naphthol (II), the *N*-acetyl derivative (III) of I, and 4-X-2:5-diacetamido-1-naphthol (IV), where—

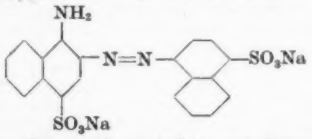


proved that only alkaline solutions of I, III, and IV, not II, are titratable with hydrochloric acid, the first three giving inflections at, respectively, pH 9 and 5·2, 8·8 and 4·2, and 9·2 and 5·1. Consequently, only the hydroxyl group *para* to the azo group is titratable. The absorption maximum of I moves from 510 mμ. at pH 3 to 530 mμ. at pH 5 (0·07% ionisation), 550 mμ. at pH 7, and 580 mμ. at pH 9 (almost complete ionisation). An analogous shift of the maximum occurs with III. The absorption spectrum of completely ionised I is close to that of II. The hydroxyazo dyes are resonance systems in which, in the case of hydroxyl groups *ortho* to the azo group, a closed six-membered resonance ring is formed by hydrogen bonds. Owing to the energy gain due to this resonance, electrolytic dissociation and acid properties are suppressed. The azoid –C(N:R):C(OH)– and quinonehydrazonic –C(:N·NH·R)·C(:O)– forms of the *ortho* compounds are not tautomeric but mesomeric structures. When the hydroxyl group is *para* to the azo group, electrolytic dissociation of hydrogen ions is energetically favoured owing to formation of a high-resonance anion, hence the strongly acidic properties of these compounds. C. O. C.

Electrolytic Preparation of Azo Dyes. II— Effect on Dye Yield of Duration of Hydrolysis. V. V. Raman and M. V. Sitaram. *Current Science* (India), **18**, 44, 45 (1949): *Chem. Abs.*, **43**, 4961 (1949).

Sulphanilic acid (2·5 g.), β-naphthol (1·8 g.), sodium hydroxide (0·8 g.), and sodium nitrite (1 g.) in water (150 c.c.) were electrolysed at 5 amp./sq. dm. and the resulting Orange II was precipitated as the barium salt. The yield was 31% of the theoretical, and 55·4% of the theoretical when treble the theoretical current was used. The authors are unable to confirm Löb's claim (*Z. Elektrochem.*, **10**, 237 (1904)) that Congo Red can be prepared electrolytically, for when they electrolysed sodium naphthionate (3·06 g.), benzidine (1·15 g.), sodium nitrite (0·87 g.), and sodium hydroxide (1 g.) in water (150 c.c.)

at 60–65°c. and 5 amp./sq. dm. a red anolyte was obtained. This, on filtering, boiling the filtrate with 5 g. magnesium oxide for 20 min., cooling, and filtering yielded a reddish-black powder which gave an aqueous red solution; and this when taken up by filter-paper gave a purple spot with dilute sulphuric acid, quite distinct from that given by Congo Red paper. This dye has the formula—



Efforts were then made to isolate any Congo Red that might be present, and finally a 14% yield of Congo Red was obtained. It proved impossible to improve this yield by altering the conditions. Evidently this method of preparing benzidine dyes is restricted to types in which the coupling component has no diazotisable amino groups.

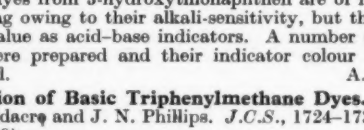
C. O. C.

Azo Dyes from 3-Hydroxythionaphthen. V. M. Rodionov, B. M. Bogoslovsky, and Z. S. Kazakova. *J. Appl. Chem.* (*U.S.S.R.*), **21**, 962–965 (Sept. 1948).

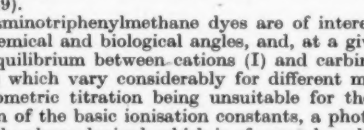
Azo dyes from 3-hydroxythionaphthen are of no value in dyeing owing to their alkali-sensitivity, but they may be of value as acid–base indicators. A number of these dyes were prepared and their indicator colour changes recorded. A. E. S.

Ionisation of Basic Triphenylmethane Dyes. R. J. Goldacre and J. N. Phillips. *J.C.S.*, 1724–1732 (July 1949).

The aminotriphenylmethane dyes are of interest from both chemical and biological angles, and, at a given pH, reach equilibrium between cations (I) and carbinols (II) at rates which vary considerably for different members. Potentiometric titration being unsuitable for the determination of the basic ionisation constants, a photometric method has been devised, which is of general applicability to the study of cations like these, which are capable of isomerisation to carbinols. In this way, the rates of carbinol formation, and the degree of ionisation at equilibrium have been determined at various pH values. The ionisation constants are found to be independent of the pH at which they were obtained and thus may be compared with those derived from a simple ionisation such as that of an aromatic amine. The significance of carbinol formation in the following substances is discussed—Doebner's Violet, malachite Green, Pararosaniline, Brilliant Green, and Crystal Violet.



(I)



(II)

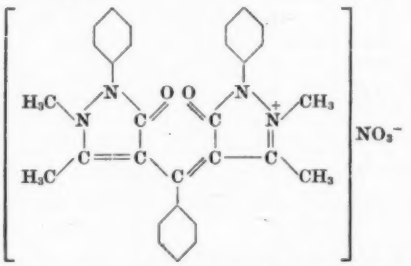
H. H. H.

Azoic Dyes. IX— Behaviour of 2-Benzoylacetyl-1-naphthol towards Diazonium Salts. N. Anand, D. M. Patel, and K. Venkataraman. *Proc. Indian Acad. Sci.*, **28A**, 545–555 (1948): *Chem. Abs.*, **43**, 5778 (1949).

Diketones obtained by treating *o*-benzoyloxyaryl methyl ketones with sodamide, potassium carbonate, or sodium ethoxide have been investigated as coupling components for azo dyes. 2-Benzoylacetyl-1-naphthol coupled with 3 mol. of diazotised aniline yielded a red disazo dye; coupled with 1 mol. of diazotised aniline it yielded not only the same disazo dye but also an orange monoazo dye; coupled with 1 mol. of diazotised 2:5-dichloroaniline it yielded a disazo dye which yielded a flavone when boiled with acetic acid; used as a "naphthol" on cotton and developed with diazonium salts it gave weak dyeings lacking fastness to soaping and light. C. O. C.

Red Dyes having Antipyrine Nuclei. A. E. Poray-Koshits, O. F. Ginzburg, and B. A. Poray-Koshits. *J. Gen. Chem.* (*U.S.S.R.*), **17**, 1752–1757 (1947): *Chem. Abs.*, **42**, 6359 (1948).

The red dye—



is obtained by treating di-4-antipyrylphenylmethane hydrochloride suspended in 4% hydrochloric acid with nitric acid until dissolved, then making alkaline with ammonia, filtering, and adding enough nitric acid to the filtrate to make it acid to Congo Red. The corresponding *p*-dimethylaminophenylcarbinol, also a red dye, is obtained by heating di-4-antipyryl-*p*-dimethylaminophenylmethane dihydrochloride in 10% aqueous ferric chloride for 1·5 hr. at 80–85°c., cooling, adding enough caustic soda to precipitate the iron, filtering, and adding 20% caustic soda until the red colour vanishes and the dye is precipitated. C. O. C.

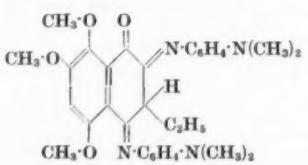
Indoaniline Dyes. III— Coupling of *p*-Substituted Phenols with Oxidised *p*-Aminodimethylaniline. P. W. Vittum and G. H. Brown. *J. Amer. Chem. Soc.*, **71**, 2287–2290 (1949).

Many *p*-substituted phenols do not couple with oxidised *p*-aminodimethylaniline to produce indoaniline dyes. Those bearing *p*-Hal, -COOH, $-SO_3H$, -OR, $-R\cdot CH(OH)$, or $-R^1CR^2$ groups react more or less readily to yield *p*-indoaniline dyes by elimination of the *p*-substituent. The ease with which the elimination coupling occurs appears to be influenced by the presence of other substituents in the phenol ring. No evidence of *o*-indoaniline dye formation has been observed with any of the phenols studied.

C. O. C.

***Echinoidea* Dyes. II—2-Ethyl-3:5:6:8-tetrahydroxy-1:4-naphthaquinones.** O. Brunner and E. Singule. *Monatsh.*, **79**, 81–86 (1948): *Chem. Abs.*, **43**, 2608, 2609 (1949).

2:4:5-Trimethoxybenzaldehyde is prepared in 61% yield from zinc cyanide, hydrochloric acid, aluminium chloride, and 1:2:4-trimethoxybenzene. This with methyl *α*-bromopropionate by the Reformatsky reaction gives ethyl 2:4:5-trimethoxy-*α*-ethylcinnamate, which by a Bouveault–Blanc reduction gives 2-(2′:4′:5′-trimethoxybenzyl)-1-butanol. Substitution of CN for OH gives *β*-(2:4:5-trimethoxybenzyl)valeronitrile, which is saponified to *β*-(2:4:5-trimethoxybenzyl)valeric acid. Heating this with 85% sulphuric acid gives 3-ethyl-5:7:8-trimethoxy-3:4-dihydro-1(2H)-naphthalenone. This with *p*-nitrosodimethylaniline passes through the intermediate product—



into 2-ethyl-3-hydroxy-5 : 6 : 8-trimethoxy-1 : 4-naphthaquinone, which on demethylation yields 2-ethyl-3:5:6:8-tetrahydroxy-1:4-naphthaquinone as red crystals, m.p. 190–192°c. C. O. C.

Acid Anthraquinone Derivatives— I. M. K. Bezzubets and V. S. Rozina. *J. Appl. Chem.* (*U.S.S.R.*), **21**, 1152–1161 (Nov. 1948).

A study is made of a group of ten anthraquinone acid dyes of the general formula 1-amino-4-arylaminoanthraquinone-2-sulphonic acid, where the nucleus of the arylamino radical contains various methyl and chlorine substituents. The absorption spectrum in solution is recorded, and the colours of dyeings on wool are described. The fastness of the dyeings to light, water, washing, milling, perspiration, rubbing, and other agencies is measured. A theoretical discussion is given of the relation between colour and constitution in this group of dyes.

A. E. S.

Preparation of Anthraquinone Vat Dyes by Alkali Fusion. I— Influence of Amounts of Added Soyabean Protein on Formation of Indanthrone. Y. Shimada. *J. Soc. Chem. Ind. Japan*, **45**, 6–8 (1942): *Chem. Abs.*, **43**, 5189 (1949).

In treating 2-aminoanthraquinone with molten potassium and sodium hydroxides to produce indanthrone, addition of soyabean protein to the molten alkali accelerated the reaction and increased the yield. This was caused mainly by the improved wetting power of the raw material in the molten alkali, with consequent prevention of its sublimation. The best yield, 41·4%, was obtained by fusing 5 g. of 2-aminoanthraquinone with 10 g. each of potassium and sodium hydroxides and 4 g. of soyabean protein at 230°c. for 15 min.

II— Influence of Temperature, Time, Proportion of Sodium Hydroxide to Potassium Hydroxide and Water on the Indanthrone Fusion. *Ibid.*, **46**, 814–817 (1943): *Chem. Abs.*, **43**, 5189 (1949).

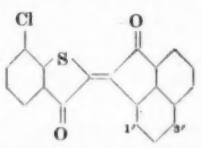
The influence of the above factors on formation of (1) reaction product soluble in alkali, (2) portion soluble in alkaline hydrosulphite solution, and (3) pure indanthrone, was studied. Best results were obtained by fusing 10 g. sodium hydroxide (92%), 10 g. potassium hydroxide (85%), 50 g. 2-aminoanthraquinone, and 4 g. soyabean protein at 230°c. for 20 min. to yield 42% indanthrone. Use of sodium hydroxide is desirable even when it constitutes $> 50\%$ of the mixed alkali but above 70% of sodium hydroxide the fusion cannot be carried out smoothly. Influence of temperature and time is small, but that of water is considerable.

III— Function of Soyabean Protein as an Addition Agent in the Indanthrone Fusion. *Ibid.*, **46**, 817–820 (1943): *Chem. Abs.*, **43**, 5189 (1949).

Soyabean protein selectively accelerates formation of indanthrone and in presence of soyabean protein 2-aminoanthraquinone is readily wetted by molten alkali. Confirmation has been obtained that in the indanthrone fusion leucine has a very important rôle. The value of soyabean protein in this fusion is mainly due to its leucine content. C. O. C.

Dyes derived from Acenaphthenequinone. X— 2-(7-Chloro)-Thionaphthene-Acenaphthylene Indigos. S. K. Guha and J. N. Chatterjee. *J. Indian Chem. Soc.*, **25**, 429–432 (Sept. 1948).

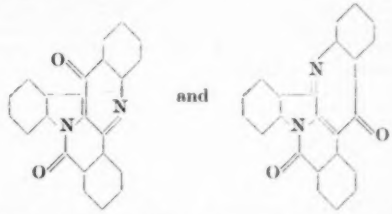
Acenaphthenequinone and its 3-chloro-, 3-bromo-, and 1-methoxy-derivatives have been condensed with 7-chloro-3-hydroxythionaphthen, and a new series of thioindigoid vat dyes obtained of asymmetrical character and of formula—



These are yellowish-red, red, and deep red crystalline compounds, soluble in pyridine, xylene, and nitrobenzene. The vat is produced at 50–60°c. by alkaline hydrosulphite; excess alkali causes a tarry product to be formed. The dyeings on cotton (red, red, deep red, and pink, respectively) are lighter than those of the corresponding dyes in the 2 - (5 - chloro) - thionaphthen – acenaphthyleneindigo series. The dyeings on wool from a dilute sulphuric acid bath are uniform. 2 - (7 - Chloro) - thionaphthen - 1'-acenanthryleneindigo is brown. H. H. H.

Benzoylated Derivatives of Indigo— IX. H. de Diesbach, M. Capponi, and J. Farquet. *Helv. Chim. Acta*, **32**, 1214–1227 (June 1949).

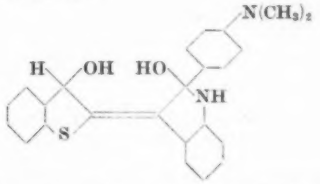
New formulæ are proposed for Indigo Yellow 3G and Höchst Yellow U—



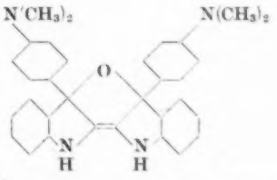
which contain an indole and a seven-membered heterocyclic nucleus. Evidence is presented in favour of these structures and, in particular, for the presence of an indole nucleus. A new preparative route is also described for the derivatives of the quindoline, obtained formerly by the action of aromatic amines on the Dessoulavy compound, which has enabled the determination of their true formulæ. Included also are a series of products derived from the lactam obtained by the condensation of phthalaldehydic acid with indoxyl. H. H. H.

Comparative Tests in the Indigoid Series. H. de Diesbach and E. Heppner. *Helv. Chim. Acta*, **32**, 687–691 (May 1949).

The differences which indigo, indirubin, phenyl*iso*indigo, diphenyl-1:1'-*iso*indigo, Thioindigo Scarlet, and thioindigo exhibit towards acylation, hydrazine, acid reducing agents, and dimethylaniline are described. Only indigo has its constitution modified by benzoylation to give Dessoulavy compounds, the other indigoids behaving normally. Indigo gives desoxy indigo with hydrazine, but indirubin first forms a hydrazone, which cyclises to a spiran; and *iso*indigo, Thioindigo Scarlet, and thioindigo are reduced to their leuco derivatives. Indigo is ruptured by metals in acid solution at the pyrrole nuclei, indirubin gives indileucine, while the other indigoids form leuco derivatives. Thioindigo does not react with dimethylaniline; *iso*indigo is degraded; Indigo Scarlet gives a colourless derivative—



which lead peroxide oxidises to a red product in which the –CH(OH)– of the sulphur ring has become a keto group; while indigo condenses in the presence of aluminium chloride to give Haller and Guyot's product (*Compt. rend.*, **144**, 947 (1907))—



whose formula is now verified; indirubin gives an analogous product. H. H. H.

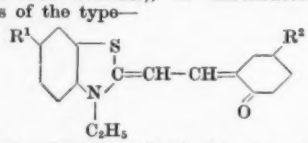
Studies in Indigoid Dyes. XI— Phenanthrathiopheneindigo. P. C. Dutta. *J. Indian Chem. Soc.*, **26**, 27–30 (Jan. 1949).

The preparation of 9:10-phenanthra-2'-ketodihydrothiophen from 9-thiolphenanthrene is described. When it is

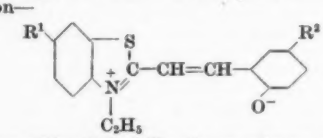
oxidised and condensed with phenanthraquinone, bis-9:10-phenanthrathiophen–indigo is formed, which dyes cotton brown. The dyes prepared by condensation with acenaphthaquinone or isatin dye cotton red. These hues conform to the author's previous findings. A. S. F.

Effect of the Solvent on the Colour of Organic Dyes—II. A. I. Kiprianov and E. S. Timoshenko. *J. Gen. Chem.* (*U.S.S.R.*), **17**, 1468–1476 (1947): *Chem. Abs.*, **42**, 8475–8478 (1948).

Observed shifts of the absorption maximum, depending on the polarity of the solvent (water and ethyl alcohol or chloroform and benzene), of substituted intraïnoid derivatives of the type—

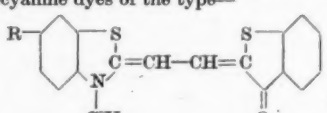


(R^1 and $R^2 = O{\cdot}C_2H_5$ and $N(CH_3)_2$, i.e. electron-donor groups, or NO_2, electron-acceptor) confirm the assumption that such shifts are attributable to displacements of resonance between the above non-polar form and the dipolar ion—

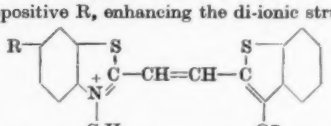


An electropositive R^1 shifts the maximum to shorter, an electronegative R^1 to longer, wavelengths. On the other hand, an electropositive R^1 favours the dipolar-ion form, an electronegative R^1 the non-polar form. In contrast thereto, a positive R_2 should favour the non-polar form, a negative R_2 the ionic form; accordingly a positive R_2 shifts the maximum to longer, a negative R^2 to shorter, wavelengths. Substitution of a positive R^1 and a negative R^2 results in an accumulated strong hypsochromic effect.

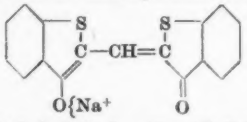
In *mero*cyanine dyes of the type—



an electropositive R, enhancing the di-ionic structure—



shifts the colour towards the red side, and electronegative R has the opposite effect. The hypsochromic shifts due to perturbation of equivalence of resonance forms of an asymmetric dye can be calculated from the absorption maximum of two symmetrical "mother" dyes, e.g. from absorption data for thiocarbocyanines and for oxanin—



the shifts in ethyl alcohol when R = H, $O{\cdot}C_2H_5$, $N(CH_3)_2$, $\overset{+}{N}H(CH_3)_2$, or NO_2 are, respectively, 20, 18·5, 15, 68, and 45·5 mμ., i.e. the inequality of the non-polar and the di-ionic forms is decreased by positive R and sharply increased by negative R.

The syntheses of a large number of dyes used for this work are described. C. O. C.

Resonance and Polarity in the Molecules of Three Coloured Compounds. L. M. Kushner and C. P. Smyth. *J. Amer. Chem. Soc.*, **71**, 1401–1406 (1949).

The *mero*cyanines are unionised dyes characterised by the amidic resonating system—

$$>N\text{–}[\overset{|}{C}=\overset{|}{C}]_n\text{–}\overset{|}{C}=O \longleftrightarrow >\overset{+}{N}=[\overset{|}{C}\text{–}\overset{|}{C}]_n=\overset{|}{C}\text{–}\overset{-}{O}$$

Measurement of the dipole moments of three dyes of this series — viz. 3-ethyl-5-[4-(1-ethyl-3 : 3-dimethyl-2(3)-indolylidene)-butenylidene]-rhodanine, 1:3-diethyl-5-[4-(1-ethyl-3:3-dimethyl-2(1)-indolylidene)-2-butenylidene]-2-thiobarbituric acid, and 1:3-diethyl-5-[1:3-diethyl-2(3)-benzimidazolylidene)-butenylidene]-barbituric acid— in very dilute solutions shows that one molecule receives a contribution from one polar structure, one from two polar structures, and one from four polar structures. The large dipole moments increase as the number of contributing polar structures increases, to such an extent that the moment of the molecule with four contributing polar structures is larger than that previously found for any molecule except that of a salt or a zwitterion. The dipole moment values qualitatively confirm predictions of the relative polarities of the substances and make possible exact calculations of the relative contributions of the polar structures. The absolute amounts of these contributions are calculated on the basis of reasonable values for the moments of the polar structures. A quantum-mechanical calculation of the relative energies of the structure explains the quantitative deviations from the amounts of the contributions to be expected merely on the basis of the number of contributing polar structures. C. O. C.

Crystalline Methylpteridine Red. P. Karrer and R. Schwyzer. *Helv. Chim. Acta*, **32**, 1689–1692 (Aug. 1949).

Methylpteridine Red is formed by heating pure 2-amino-6-hydroxy-8-methylpteridine with 20% sulphuric acid in the air, or with exclusion of air, in good yield as a dark violet powder which possesses a green surface lustre. On extraction with boiling water, the crude product loses by degrees its bound sulphuric acid and becomes a bright red powder, which by crystallisation from 2 N. hydrochloric acid is obtained in small crystals having no m.p. Both cotton and wool are dyed a bright red from a 0·05% hydrochloric acid bath, the cotton being turned to red–blue by aftercoppering and the wool to brown–yellow by afterchroming. The dyed wool fluoresces pale blue under the fluorescence lamp, and the cotton intense yellow. H. H. H.

[**Italian**] **Bitumens as Pigments.** E. Cianetti. *Pitture e Vernici*, **4**, 71–74 (1948): *Chem. Abs.*, **43**, 5178 (1949).

Aluminium Flake Powder—Nature and Rôle of Leafing. G. W. Wendon. *Paint*, **19**, 265–271, 286 (1949).

Barium Potassium Chromate Pigment in Metal-protective Paint. A. J. Eickhoff and L. M. Kebrich. *Official Digest Federation Paint and Varnish Production Clubs*, (291), pp. 188–198: *Chem. Abs.*, **43**, 5604 (1949).

Principal Factors influencing Photodegradation of Dyes. J. Pinte and J. Millet. *Teintex*, **14**, 21–33 (Jan. 1949).

A review of the literature under three main headings—degradation of dyes by oxidation, combined action of substrate and dye, and specific action of spectral radiations. B. K.

PATENTS

Diazotype Materials derived from Aryl Diazosulphones. J. A. Sprung, W. A. Schmidt, and General Aniline & Film Corpn. *U.S.P.* 2,465,760.

Diazosulphones of general formula $R^1{\cdot}N{:}N{\cdot}SO_2{\cdot}R^2$ (R^1 = an aromatic radical, R^2 = an aliphatic or aromatic radical), e.g. *p*-acetoamidophenyl 2:5-diethoxy-4-benzamidodiazosulphone, are used as the light-sensitive agent in diazotype materials. The example given above used with 2:3-dihydroxynaphthalene as the coupling component gives a purple image. C. O. C.

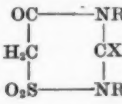
Coupling Component for Blues on Diazotype Papers. General Aniline & Film Corpn., W. H. von Glahn, and L. N. Stanley. *B.P.* 624,472.

2:8-Dihydroxynaphthalene-6-sulphonic acid is used as the coupling component in diazotype printing papers with any of the usual diazo components, e.g. stabilised diazotised *N*-substituted *p*-phenylenediamines. The papers so treated have good storage properties; the hues obtained

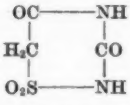
vary from dark blue to reddish blue, and have very good light fastness and good wash fastness. C. H. G.

Six-membered Heterocyclic Compounds — Dye Intermediates. J. B. Dickey and Eastman Kodak Co. *U.S.P.* 2,466,396.

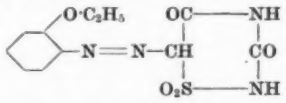
Compounds of general formula—



(X = oxygen or sulphur; R^1 and R^2 each = hydrogen, an alkyl group having 1–4 carbon atoms, a hydroxyalkyl group having 2–3 carbon atoms, an alkoxyalkyl group having 3–4 carbon atoms, a phenyl or a benzyl group) couple with aromatic diazonium compounds to form dyes. Thus—



when coupled with *o*-phenetidine yields azo dye—



which dyes acetate rayon and nylon yellow from aqueous suspension. C. O. C.

Phthalideneacetamides—Dye Intermediates. R. M. Leekley and Du Pont. *U.S.P.* 2,472,666.

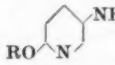
Phthalideneacetamides and their acetals with alkanols of 1–4 C and 1:2- and 1:3-alkanediols of 2–4 C are useful as dye intermediates or as photographic colour formers. Coupled with diazonium salts they enable a water-solubilising group to be introduced into dyes which hitherto could not be rendered water-soluble. They may be obtained by treating phthalideneacetyl chlorides with primary or secondary amines. C. O. C.

Phthalimido Derivatives of Pyridine and its Salts. Pyridium Corpn. *B.P.* 625,429.

2-R-oxy-5-phthalimidopyridines (R = an alkyl or alkyloxyalkyl group containing < 9 carbon atoms, a homocyclic, heterocyclic, aminoaryl, aminoaralkyl, aryloxyalkyl, or aralkyloxylated group) are obtained by treating the corresponding amino compound with excess phthalic anhydride in an inert solvent. They are stable solids, whereas the corresponding bases are unstable liquids. Thus 2-hexyloxy-5-phthalimidopyridine, a white solid whose alkali metal salts are water-soluble, is obtained by refluxing 2-hexyloxy-5-aminopyridine and phthalic anhydride in methanol. They are useful dye intermediates. C. O. C.

***N*-Substituted 2-Alkoxy-5-aminopyridines.** Pyridium Corpn. *B.P.* 625,327.

N'-Substituted 2-R-oxy-5-aminopyridines are obtained by treating a compound of general formula—



(R = a saturated or unsaturated alkyl or alkoxyaryl radical containing < 9 carbon atoms) with an aromatic aldehyde, e.g. 2-butoxy-5-benzylideneaminopyridine from 2-butoxy-5-aminopyridine and benzaldehyde. They are more stable than the original base and so are useful as dye intermediates. C. O. C.

Resorcinolcarbonamides as Coupling Components for Diazotype Prints. F. W. Neumann and General Aniline & Film Corpn. *U.S.P.* 2,467,358.

Amides of resorcinolmonocarboxylic acids, e.g. *N*-β-hydroxyethyl-α-resorcylamide, when used in diazotype compositions are more stable to coupling than resorcinol. They yield dark-toned prints. C. O. C.

New Intermediates from Dibenzanthrone and *iso*-Dibenzanthrone. S. Coffey, F. Lodge, J. Wardleworth, and I.C.I. Ltd. *B.P.* 623,998.

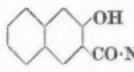
Dibenzanthrone, *iso*dibenzanthrone, or their halogen substitution products are bromo- or chloro-methylated with dichlorodimethyl ether (which may be formed *in situ* in the reaction mixture, from e.g. paraformaldehyde and hydrogen chloride) or dibromodimethyl ether in presence of either aluminium chloride and a tertiary base, e.g. pyridine, or sulphuric acid. C. H. G.

***iso*Dibenzanthrone.** M. Scalera, W. S. Forster, and American Cyanamid Co. *U.S.P.* 2,468,606.

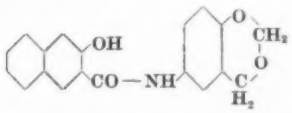
Improved yields of *iso*dibenzanthrone are obtained by heating at approx. 115–140°C. a mixture whose sole significant ingredients are 3:3'-dibenzanthronyl sulphide, > 2 mol. of alkali-metal alkoxide per mol. of sulphide, and an aliphatic alcohol containing < 7 carbon atoms. C. O. C.

***N*-Substituted Amides of 2-Hydroxy-3-naphthoic Acids.** H. P. Orem, F. H. Adams, J. P. Goulding, and American Cyanamid Co. *U.S.P.* 2,465,979.

Compounds of general formula—



(X = a benzo-1:3-dioxan or benzo-1:4-dioxan radical linked in the 6 position), e.g.—



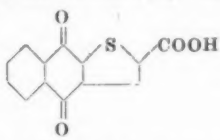
(obtained from 6-amino-1:3-benzodioxan and 2-hydroxy-3-naphthoyl chloride), readily couple with diazo compounds to produce dyes of good wash and light fastness and marked resistance to bleeding, particularly in oils. C. O. C.

Flavanthrones. H. Z. Lecher, M. Scalera, W. S. Forster, and American Cyanamid Co. *U.S.P.* 2,468,599.

Excellent yields of flavanthrones are obtained from β-aminoanthraquinones by using titanium tetrachloride or tetrabromide as the condensing agent, the reaction proceeding smoothly at 100–175°C. C. O. C.

Thiophanthraquinone-2-carboxylic Acid. V. Weinmayr and Du Pont. *U.S.P.* 2,472,133.

Thiophanthraquinone-2-carboxylic acid—



useful as a starting material for the preparation of dyes, is obtained by heating thiophanthraquinone with carbon tetrachloride in presence of a Friedel–Crafts condensation catalyst at 150–220°C., hydrolysing the product with caustic alkali, filtering to remove the unreacted thiophanthraquinone and the dithiophanthraquinonyl ketone, and acidifying the filtrate to precipitate the thiophanthraquinone-2-carboxylic acid. C. O. C.

Cyanine Dye Intermediates. A. W. Anish and General Aniline & Film Corpn. *U.S.P.* 2,453,738.

Hydrophilic Dye Intermediates. D. W. Woodward and Du Pont. *U.S.P.* 2,473,403.

Acylacetanilides for Colour Photography. Du Pont. *B.P.* 627,353.

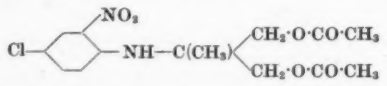
Nitrophenylaminoethyl Esters—Yellow Dyes for Acetate Rayon, Wool, Nylon, Vinyon, etc. J. G. McNally, J. B. Dickey, and Eastman Kodak Co. *U.S.P.* 2,469,695.

Compounds of general formula—

$$B{\cdot}NH{\cdot}CR^1R^2{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}Y$$

(B = a mononitrated non-sulphonated benzene nucleus, which may have one more substituent other than an

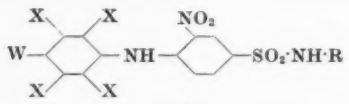
additional nitro or sulpho group; R^1 and R^2 each = an alkyl, hydroxymethyl, or $-CH_2\cdot O\cdot CO\cdot Y$ group, and R^1 may = hydrogen; Y = alkyl, alkoxyalkyl, monocyclic benzene, furyl, or alkyl group) are yellow dyes of excellent fastness to light and non-subliming for acetate rayon, wool, silk, nylon, Vinyon, and polymeric materials containing an ethylenic linkage, and are also suitable for use in cellulosic lacquers. Thus the dye—



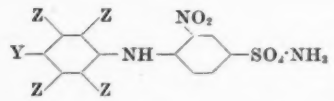
is obtained by refluxing 19·2 g. 2:5-dichloronitrobenzene, 50 c.c. butanol, and 10·5 g. 2-amino-2-methyl-1:3-propanediol with 5·5 g. sodium carbonate. The mixture is then steam-distilled, and the distillate cooled to room temperature and filtered to yield 3 g. 2-(*o*-nitro-*p*-chlorophenylamino)-2-methyl-1:3-propanediol. This (4 g.) was heated for 90 min. on an oil-bath with 10 c.c. glacial acetic acid and 10 c.c. acetic anhydride, and the mixture poured into water to precipitate the dye, which was then recrystallised from ethyl alcohol and water. C. O. C.

Nitrodiphenylamine Compounds containing a Sulphamyl Group— Dyes for Organic Derivatives of Cellulose, Wool, Silk, Nylon, Vinyon, etc. J. B. Dickey, J. G. McNally, and Eastman Kodak Co. *U.S.P.* 2,466,010.

Compounds of general formulæ—



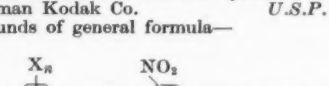
and



(R = an alkyl, hydroxyalkyl, alkoxyalkyl, monohydroxyalkoxyalkyl, monosulphoalkyl, monosulphatoalkyl, allyl, *cyclo*hexyl, tetrahydrofurfuryl, or benzyl group; W and X each = hydrogen, alkyl, hydroxy, halogen, alkacylamino, or hydroxyalkoxy, or X = an alkoxy group, no more than three of the members W and X being other than hydrogen; Y and Z = hydrogen, hydroxy, halogen, alkacylamino, or hydroxyalkoxy group or Z = an alkoxy group, at least one but not > 3 of the members Y and Z being other than a hydrogen atom) dye organic derivatives of cellulose, e.g. acetate rayon, yellow at a good dyeing speed to yield dyeings of good light fastness. They also have affinity for non-vegetable fibres, e.g. wool, silk, nylon, etc., this being especially the case if they contain a sulphoalkyl or sulphatoalkyl group. C. O. C.

Nitrodiphenylamine Compounds containing a Di-substituted Sulphamyl Group— Dyes for Organic Derivatives of Cellulose and Non-vegetable Fibres. J. B. Dickey, J. G. McNally, and Eastman Kodak Co. *U.S.P.* 2,466,011.

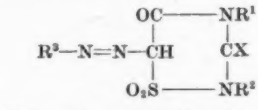
Compounds of general formula—



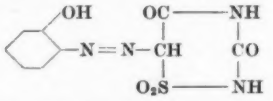
(R^1 and R^2 each = alkyl, hydroxyalkyl, alkoxyalkyl, monohydroxyalkoxyalkyl, monosulphoalkyl, monosulphatoalkyl, or allyl; X = alkyl, alkoxy, hydroxy, halogen, alkacylamino, or hydroxyalkoxy; n = 0–3) are yellow dyes of good fastness to light for organic derivatives of cellulose. They also possess affinity for wool, silk, nylon, Vinyon, and other non-vegetable fibres, this being particularly marked if they contain a sulphoalkyl or sulphatoalkyl group. C. O. C.

Heterocyclic Monoazo Dyes for Acetate Rayon, Cotton, Wool, Silk, or Nylon. J. B. Dickey and Eastman Kodak Co. *U.S.P.* 2,466,397.

Dyes of general formula—



(R^3 = the residue of a monocyclic aryl nucleus of the benzene series; R^1 and R^2 each = hydrogen, an alkyl group having 1–4 carbon atoms, a hydroxyalkyl group having 2–3 carbon atoms, an alkoxyalkyl group having 3–4 carbon atoms, a phenyl, or a benzyl group; X = oxygen or sulphur), e.g.—



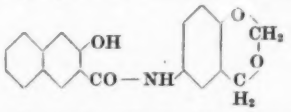
yield dyeings of good fastness to light and washing on acetate rayon. They also have affinity for cotton, wool, silk, and nylon. C. O. C.

Azoic Dyes. H. Z. Lecher, F. H. Adams, and American Cyanamid Co. *U.S.P.* 2,468,600.

The 2-ethyl-4-chloroanilide of 2-hydroxy-3-naphthoic acid couples with the diazo compounds commonly used in the azoic field to give pigments resistant to "bleeding" in the solvents used in the formulation of printing inks, etc. Coupling may also be carried out on textile fibres to give fast-to-light dyeings and prints. E. S.

Azoic Pigments containing a Dioxan Nucleus. H. P. Orem, F. H. Adams, J. P. Goulding, and American Cyanamid Co. *U.S.P.* 2,468,457.

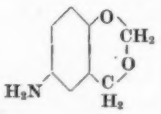
Pigments having high resistance to the solvent action of oils, lacquer solvents, varnish, etc. are made by coupling suitable diazo compounds with the benzo-1′:3′-(or 1′:4′-) dioxan-6′-amides of 2-hydroxy-3-naphthoic acid. Hence they are of particular interest for use in surface coatings, but may also be produced on textiles as azoic dyes and prints. Thus, by treating a mixture of 2-hydroxy-3-naphthoic acid and 6-amino-1:3-benzodioxan in chlorobenzene with phosphorus trichloride, the amide—



is produced. It couples with diazotised 2-amino-4-chloroanisole to give a bluish-red print on cotton. E. S.

Monoazo Dyes derived from Aminobenzodioxan. G. C. Strouse and Allied Chemical & Dye Corpn. *U.S.P.* 2,468,277.

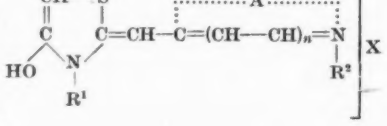
Aminodioxans, and particularly 6-amino-1:3-benzodioxan—



can be diazotised and coupled with a variety of coupling components to give monoazo dyes. Thus, with phenol, a yellow acetate rayon dye is produced, and with salicylic acid a chromable yellow wool dye. E. S.

Monoazo Dyes containing a Thiazolone Cyanine Dye Component. T. R. Thompson and General Aniline & Film Corpn. *U.S.P.* 2,464,785.

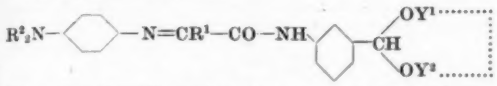
Thiazolone cyanine dyes of general formula—



(A = the atoms necessary to complete a heterocyclic nitrogenous nucleus of the type common in cyanine dyes; R^1 = alkyl, allyl, aryl, or aralkyl; R^2 = alkyl or aralkyl; n = 0 or 1; X = an acid radical) may be coupled with diazonium compounds, in substance or on the fibre. The dyes so produced find application in colour photography as well as in textile dyeing. E. S.

Azomethine Dyes from Acylacetamidobenzaldehyde Acetals. D. M. McQueen and Du Pont. *U.S.P.* 2,472,913.

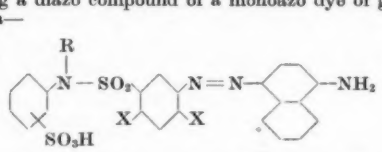
Dyes of general formula—



(R^1 = a carboxylic acyl radical of < 12 C directly connected to the azomethine carbon atom by the carbonyl group of the acyl radical; R^2 = an alkyl radical of 1–4 C; Y^1 and Y^2 = alkyl radicals of 1–4 C and when joined form a saturated aliphatic bivalent hydrocarbon radical of 2–4 C where 2–3 atoms are in the chain between the two oxygen atoms) are brilliant yellow vat dyes of excellent fastness to washing. C. O. C.

Blue Disazo Acid Dyes. Ciba Ltd. *B.P.* 626,916.

Violet–blue and navy blue acid dyes are made by coupling a diazo compound of a monoazo dye of general formula—



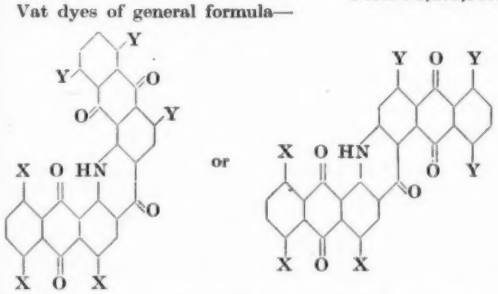
(R = methyl or ethyl; one X = H, and the other X = H, methyl, or halogen) with a 1-arylaminonaphthalene-8-sulphonic acid. E. S.

Benzanthrone–Acridine Vat Dye. L. D. Lytle and American Cyanamid Co. *U.S.P.* 2,456,589.

Crude chlorobenzanthrone is condensed with 1-aminoanthraquinone to give a greenish-grey vat dye fast to light and hydrogen peroxide. R. K. F.

Diaminodianthrimide - Acridone Vat Dyes. M. Scalera, A. W. Joyce, and American Cyanamid Co. *U.S.P.* 2,468,605.

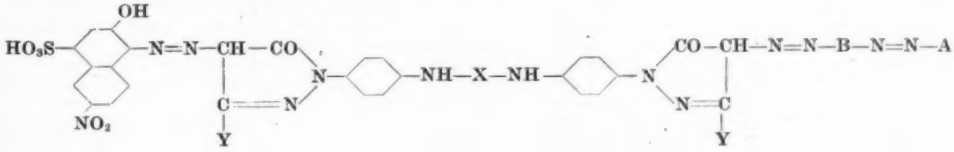
Vat dyes of general formula—



(X and Y = hydrogen, amino, or acylamino radicals, at least one X and one Y being amino or acylamino) dye cellulosic fibres brown to grey to olive from violet vats. They may be obtained by ring closure of diacylaminodianthrimides bearing a carboxy or cyano group *ortho* to the imino linkage by heating in concentrated sulphuric acid. C. O. C.

Metallisable, Substantive Polyazo Dyes. J. R. Geigy A.-G. *B.P.* 627,069.

Substantive polyazo dyes, which may be metallised in substance or on the fibre, of general formula—



(X = –CO– or –CS–; Y = alkyl, phenyl, carboxyl, or substituted carboxyl; B = the radical of a tetrazotised aromatic diamine; A = the radical of any desired coupling component, which may also contain one or more azo groups) may be synthesised in a variety of ways. Thus, all parts being by weight, 4:4′-diaminodiphenylurea (24·2) is tetrazotised and coupled in presence of sodium bicarbonate with the monoazo dye (139·8) obtained by coupling 1 mol. of diazotised 1-amino-6-nitro-2-naphthol-4-sulphonic acid with 1 mol. of the urea of 1-*p*-aminophenyl-3-methyl-5-pyrazolone. The polyazo dye so formed dyes cellulosic fibres brown–red, converted to red, fast to light and water, by aftertreatment with copper salts. E. S.

4-Alkylquinolines. K. N. Campbell and Du Pont. *U.S.P.* 2,451,610.

The hydrogen halide of a primary arylamine having at least one free *ortho* position is condensed with an alkyl vinyl ketone in presence of ferric chloride as oxidising agent. *U.S.P.* 2,451,611.

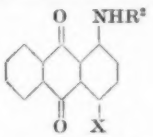
A primary arylamine with at least one free *ortho* position is condensed with a 1:3:3-trialkoxyalkane in presence of ferric chloride. R. K. F.

New Anthraquinone Dyes for Acetate Rayon and Nylon. Kodak Ltd., H. W. Coover, J. B. Dickey, and E. B. Towne. *B.P.* 626,704.

A compound of general formula—

$$NH_2{\cdot}Q{\cdot}O{\cdot}D{\cdot}[O{\cdot}D]_n{\cdot}O{\cdot}R^1$$

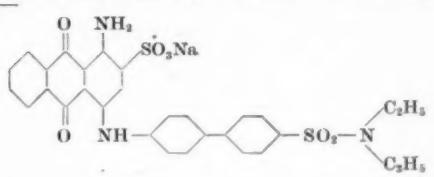
is heated with a compound of general formula—



either (*a*) where X = OH, (*b*) where X = Hal, in presence of an ammonium salt of a lower fatty acid, a copper catalyst, and an acid condensing agent, or (*c*) with the leuco derivative where X = NHR^2. The products in which X = $NH{\cdot}Q{\cdot}O{\cdot}D{\cdot}[O{\cdot}D]_n{\cdot}O{\cdot}R^1$ (n = 1 or 2; R^1 = hydrogen or a methyl or ethyl group; R^2 = an alkyl, alkoxyalkyl, or hydroxyalkyl group containing < 5 carbon atoms; D = an ethylene, a trimethylene, or a propylene group; Q = an *o*- or *p*-phenylene group, substituted or unsubstituted) are insoluble blue–green dyes for cellulose carboxylic esters (e.g. cellulose acetate) or nylon fibres, of improved fastness to light and burnt gas fumes. C. H. G.

Anthraquinonoid Acid Dyes. Allied Chemical & Dye Corpn. *B.P.* 626,446.

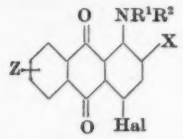
1-Amino(or substituted amino)anthraquinonesulphonic or -carboxylic acids containing halogen in the 4-position are condensed with an aminodiphenylsulphonamide to give blue to green neutral-dyeing acid dyes. Thus, sodium 1-amino-4-bromoanthraquinone-2-sulphonate, 4-aminodiphenyl-4′-sulphondiethylamide, urea, sodium bicarbonate, and cuprous chloride are heated together in aqueous ethanol at 75°c. for about 6 hr. The mixture is then diluted with water, filtered, and purified by dissolving in aqueous ethanol and then acidifying. The resulting free acid is filtered, neutralised, and salted to produce the dye—



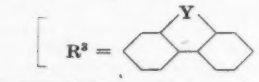
R. K. F.

Blue to Green Anthraquinone Acid Dyes. Allied Chemical & Dye Corpn. *B.P.* 610,808.

Blue to green acid dyes are obtained by condensing a compound of general formula—



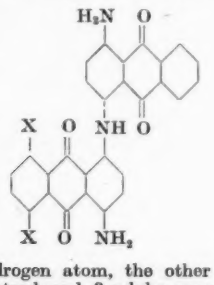
(R^1 and R^2 each = hydrogen or an alkyl, aralkyl, hydroxyalkyl, *cyclo*alkyl, aryl, hydroaryl, or heterocyclic radical; X = a carboxyl or sulpho group; Z = a carboxyl or sulpho group, or either X or Z (but not both) = hydrogen) with a compound of general formula $R^3(NH_2)_m$



(Y = O, S, NH, N Alk, or SO_2) or a hydrogenated, alkyl, alkoxy, aryl, halogen, or sulpho derivative of it; m = 1 or 2) in presence of a copper condensation catalyst. C. O. C.

Grey Acid Anthraquinone Dyes. G. M. Smyth and American Cyanamid Co. *U.S.P.* 2,454,679.

Grey acid dyes of excellent light fastness, which may be top-chromed to increase fastness, are obtained by sulphonating triaminodianthrimides of general formula—



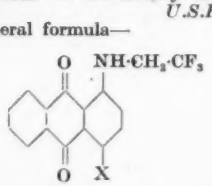
(one X = a hydrogen atom, the other X = an amino group) so as to introduce 1–3 sulpho groups. C. O. C.

Chloro- and Bromo-methylanthraquinone Derivatives. S. Coffey, F. Lodge, J. Wardleworth, and I.C.I. Ltd. *B.P.* 623,997.

Anthraquinonoid intermediates containing chloro- or bromo-methyl groups are made by treating anthraquinone derivatives containing one or more aryl groups attached directly or through –O–, –S–, –CO·NH–, or –NH– linkages, with dichloro- or dibromo-dimethyl ether, which may be formed *in situ* from e.g. paraformaldehyde and hydrogen chloride. The reaction is carried out in presence of sulphuric acid or aluminium chloride. R. K. F.

Anthraquinone Compounds containing a 2:2:2-Trifluoroethylamino Group—Dyes for Acetate Rayon and Nylon. J. B. Dickey and Eastman Kodak Co. *U.S.P.* 2,466,008.

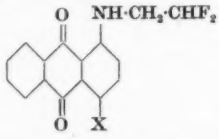
Compounds of general formula—



(X = hydrogen, bromine, chlorine, or a hydroxy, amino, 2:2-difluoroethylamino, or 2:2:2-trifluoroethylamino group, an alkylamino group containing 1–6 carbon atoms, or an alkoxyalkylamino group containing 3–8 carbon atoms in which the oxygen linkage is joined to a carbon atom, other than an α-carbon atom, of the group immediately preceding it, a hydroxyalkylamino group containing 2–5 carbon atoms and no hydroxy group on the carbon atom attached to the nitrogen atom, or a monohydroxyalkoxyalkylamino group containing 4–9 carbon atoms whose hydroxyl group is attached to a carbon atom, other than an α-carbon atom, of the alkoxy group furthest removed from the amino group, in which the $-O\cdot C_nH_{2n}-$ and $-C_nH_{2n}-$ groups present in the monohydroxyalkoxyalkylamino group contain 2 or 3 carbon atoms, and in which the oxygen linkage is to a carbon atom, other than an α-carbon atom, of the group immediately preceding it) are orange, reddish-pink, reddish-violet, violet, and reddish-blue dyes for cellulose acetate and nylon. They have excellent gas-fading and light fastness. C. O. C.

Anthraquinone Compounds containing a 2:2-Difluoroethylamino Group—Dyes for Acetate Rayon and Nylon. J. B. Dickey and Eastman Kodak Co. *U.S.P.* 2,466,009.

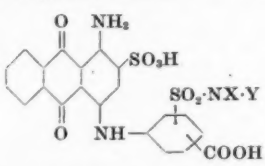
Compounds of general formula—



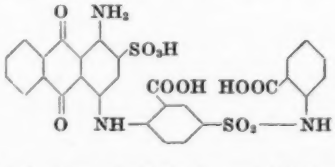
(X = hydrogen, bromine, chlorine, a hydroxyl, amino, or 2:2-difluoroethylamino group, an alkoxyalkylamino group containing 3–8 carbon atoms whose oxygen linkage is joined to a carbon atom, other than an α-carbon atom, of the group immediately preceding it, a hydroxyalkylamino group containing 2–5 carbon atoms and no hydroxyl group on the carbon atom attached to the nitrogen atom, or a monohydroxyalkoxyalkylamino group containing 4–9 carbon atoms whose hydroxyl group is attached to a carbon atom, other than an α-carbon atom, of the alkoxy group furthest from the amino group, in which the $-O\cdot C_nH_{2n}-$ and $-C_nH_{2n}-$ groups contain 2 or 3 carbon atoms, and whose oxygen linkage is joined to a carbon atom, other than an α-carbon atom, of the group immediately preceding it) are orange, reddish-pink, reddish-violet, violet, and reddish-blue dyes for organic derivatives of cellulose and nylon. They have excellent fastness to light and gas fading. C. O. C.

Aminoanthraquinonesulphonamides — Acid Dyes. C. G. Vogt and General Aniline & Film Corpn. *U.S.P.* 2,453,104.

Compounds of general formula—



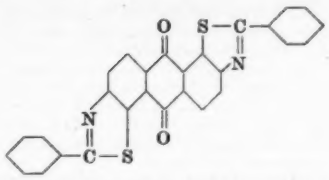
(X = H or X and Y each = a saturated aliphatic, alicyclic, or aromatic radical which may be substituted by carboxy, carbalkoxy, alkoxy, acyloxy, hydroxy, halogen, sulpho, or *sec.*- or *tert.*-alkylamino groups; or X and Y together = a bivalent alkylene radical which with the nitrogen atom on the sulphonyl group constitutes a 5–7-membered ring), e.g.—



dye wool and nylon clear blue to greenish blue from an acid bath. They are prepared by heating together in aqueous medium sodium 1-amino-4-bromoanthraquinone-2-sulphonate, and aminobenzenesulphonamide, sodium carbonate, and a copper catalyst. C. O. C.

Finely Divided Anthraquinone–Thiazole Vat Dyes. J. F. Cullinan, L. D. Lytle, and American Cyanamid Co. *U.S.P.* 2,453,410.

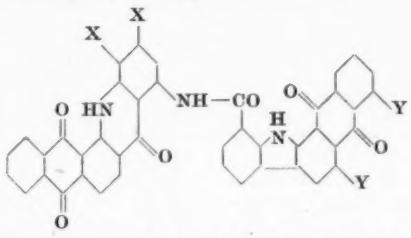
Vat dyes containing not < 1 anthraquinone and not < 1 thiazole nucleus, e.g. 1:2:5:6-bis-*C*-phenylthiazolo-anthraquinone—



are obtained in very finely divided particles of uniform size by slurrying one part of the dye with 20–30 parts of sulphuric acid, of such strength that some but not > 10% by weight of the total dye is in solution at any one time, agitating until all the dye is converted into an insoluble sulphate, and then hydrolysing it back to the dye. C. O. C.

Anthraquinone–Acridone–Carbazole Dyes. F. Max, D. I. Randall, and General Aniline & Film Corpn. *U.S.P.* 2,467,561.

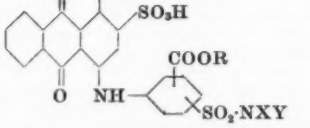
Condensing a 1:2-phthaloyl-6-*o*-halogenobenzoylaminoacridone with a 1-aminoanthraquinone which may contain a 4- or 5-benzoylamino radical and cyclising the resulting product yields vat dyes of general formula—



(X = hydrogen, alkoxy, alkyl, aryl, or halogen; Y = hydrogen or a benzoylamino radical). C. O. C.

Carbalkoxyaminoanthraquinonesulphonamides—Acid Dyes. E. E. Renfrew and General Aniline & Film Corpn. *U.S.P.* 2,453,100.

The esterification of carboxyaminoanthraquinonesulphonamides, obtained e.g. by condensing 1-amino-4-bromoanthraquinone-2-sulphonic acid with an aminobenzenesulphonamide, yields acid dyes of general formula—



(R = alkyl; X = H or X and Y = saturated aliphatic radicals or aromatic radicals of the benzene, naphthalene, or hydrogenated naphthalene series; or X and Y together = a bivalent alkylene radical which with the N of the sulphonyl group forms a 5–7-membered heterocyclic ring). They dye wool, silk, and nylon reddish blue to greenish blue with good fastness, giving deeper dyeings from neutral baths than the corresponding carboxyaminoanthraquinonesulphonamides. C. O. C.

4-Amino-1:8-naphthalimidedisulphonic Acids—Dyes for Wool and other Basic Fibres. M. Scalera, W. S. Forster, and American Cyanamid Co. *U.S.P.* 2,455,095.

The 3:*x*-disulphonic acids of 4-amino-1:8-naphthalimide dye wool and other basic fibres very brilliant yellow with strong fluorescence. They have much better exhaustion than the corresponding monosulphonic acids, greatly improved tinctorial strength, in many cases double or even greater, marked improvement in fastness to salt-water spotting, and a shift in hue from greenish yellows to warm golden yellows. These improved characteristics appear to be due to the presence of the second sulpho group, as considerable changes in other portions of the molecule do not appear to affect materially the improved characteristics. C. O. C.

Sulphonamidobenzaldehydes and Lower Acetals thereof as Colour Formers, etc. Du Pont. *B.P.* 627,125.

Tetrahydro-1-hydroxy-2- and -3-naphthamidobenzaldehydes and their Acetals with Lower Alkanols and 1:2- and 1:3-Alkanediols—Colour Formers. E. L. Martin and Du Pont. *U.S.P.* 2,472,910.

Colour Couplers for Colour Photography. Du Pont. *B.P.* 626,321.

Photographic Colour Couplers. D. B. Glass, P. W. Vittum, A. Weissberger, and Eastman Kodak Co. *U.S.P.* 2,455,170.

Cyanine, *mero*Cyanine, and Styryl Sensitising Dyes. Gevaert Photo-Producten N.V., G. Schwarz, and M. Schouwenaars. *B.P.* 625,245.

Photosensitising Dyes containing Styryl Dye Nuclei. C. D. Wilson and Du Pont. *U.S.P.* 2,465,412.

Carbocyanine Sensitising Dyes. Gevaert Photo-Producten N.V. *B.P.* 623,990.

Symmetrical and Asymmetrical *meso*-Substituted Carbocyanine Dyes. Gevaert Photo-Producten N.V. *B.P.* 625,907.

Photosensitising Dyes containing Two or More Cyanine Dye Nuclei. C. D. Wilson and Du Pont. *U.S.P.* 2,465,774.

Trinuclear Iminol Cyanine Dyes—Sensitising, Filter, and Antihalation Dyes. A. W. Anish and General Aniline & Film Corpn. *U.S.P.* 2,471,996.

Methin Photographic Sensitising Dyes. Gevaert Photo-Producten N.V. and J. Beersmans. *B.P.* 626,470.

Methin Dyes containing an *iso*Quinoline Nucleus—Photographic Sensitisers. Kodak Ltd., F. L. White, and L. G. S. Brooker. *B.P.* 625,347 and *U.S.P.* 2,466,523.

Polymethin Dyes. L. G. S. Brooker and Eastman Kodak Co. *U.S.P.* 2,454,629.

Azamethin Dyes for Photography. Kodak Ltd. and E. B. Knott. *B.P.* 625,035.

Dyes containing a Thione Group—Photographic Sensitisers. H. D. Edwards, J. D. Kendall, and Ilford Ltd. *B.P.* 624,028.

Asymmetric Oxonole Dyes for Photographic Filter, etc. Layers. Gevaert Photo-Producten N.V. *B.P.* 624,462.

Pyrimido-2′-cyanine Dyes. L. G. S. Brooker, W. F. Holcomb, C. K. Banks, and Eastman Kodak Co. *U.S.P.* 2,472,565.

Phthalocyanines. H. Z. Lecher, R. E. Brouillard, E. Baumgarten, and American Cyanamid Co. *U.S.P.* 2,460,783.

Phthalocyanine pigments are prepared by heating an *ω*-chloro- or -bromo-*o*-xylene, in which each methyl group carries at least one halogen atom, with a copper, nickel, or cobalt salt and ammonia or a substance capable of generating ammonia at the temperature used (150–250°c.). R. K. F.

Copper Phthalocyanines. R. E. Brouillard, E. Baumgarten, and American Cyanamid Co. *U.S.P.* 2,460,779.

ω-Chloro- or -bromo-*o*-tolunitriles are heated at 150–250°c. with a copper salt and ammonia or a compound capable of generating ammonia at the temperature used, to give copper phthalocyanine pigments. R. K. F.

Copper Phthalocyanine. F. H. Moser and Standard Ultramarine Co. *U.S.P.* 2,469,663.

Copper phthalocyanine pigments are obtained by heating at 150–200°c. a mixture of copper powder, urea, a catalyst, an oxidising agent, and an *o*-dicarboxylic acid or its ammonium salt, amide, imide, or anhydride or an amide of an *o*-cyanocarboxylic acid. There is 0·5 chemical equivalent of the oxidising agent per mol. of carboxylic acid or its derivative. C. O. C.

Organic Pigments. Calico Printers' Association Ltd., L. A. Lantz, A. Schofield, and E. Spinner. *B.P.* 624,491.

A finely divided polyvinylacetal of average particle size not > 3·5 *μ*., prepared by the process of *B.P.* 582,019 (cf. J.S.D.C., 63, 278 (1947)) and containing acetal groups derived from at least one aldehyde of the benzene or

naphthalene series, is dyed with a vat dye, being washed free of unfixed leuco dye before oxidation. The products are bright pigments of excellent fastness to light combined with good fastness to wet treatments. C. O. C.

Phthalocyanine-*N*-polyhydroxyalkylsulphonamides. R. L. Mayhew and General Aniline & Film Corpn. *U.S.P.* 2,459,773.

Phthalocyaninesulphonyl chlorides are condensed with polyhydroxyalkylamines to give blue water-soluble dyes for animal and vegetable fibres. R. K. F.

Copper Phthalocyanines from Phthaloyl Halides. R. J. Sumner and Roberts Chemical Co. *U.S.P.* 2,471,794.

Copper phthalocyanines are obtained by heating phthaloyl halides, the halogen atoms of which have at. wt. 35–80, with a cupriferous reagent and urea or biuret. C. O. C.

Stable Solutions of Sulphur Dyes in Organic Solvents. R. C. Conn and American Cyanamid Co. *U.S.P.* 2,472,052.

Stable liquid compositions are obtained by heating a sulphur dye with a monohydroxyalkylamine of general formula $HO{\cdot}R{\cdot}NH_2$ (R = an alkylene group of < 6C) until the dye is reduced and dispersed. The amount of amine should be sufficient to reduce the dye and maintain it in the reduced form, to dissolve the reduced dye, and to render the composition freely fluid. C. O. C.

Phthalocyanine Pigments. A. Siegel and Du Pont. *U.S.P.* 2,452,606.

Phthalocyanine pigments which do not separate or flocculate when used in coating compositions are made by having present during the condensation of aryl-*o*-dinitrile and metallic salt at 150–300°c. a white anhydrous pigment metal oxide, e.g. titanium oxide. R. K. F.

Phthalocyaninesulphonamidopyridine Derivatives. A. L. Fox and General Aniline & Film Corpn. *U.S.P.* 2,459,771.

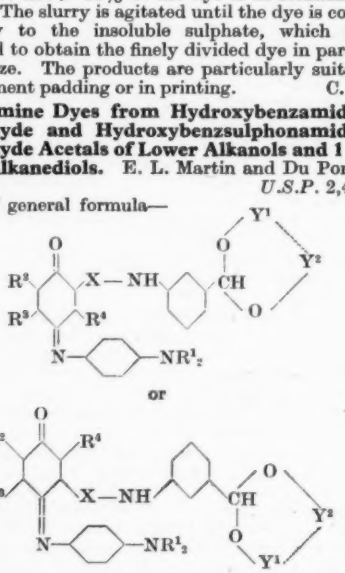
Phthalocyaninesulphonyl chlorides are condensed with heterocyclic compounds containing a primary or secondary amino group attached to or forming part of the ring, to give blue dyes soluble in dilute alkali and having affinity for animal and vegetable fibres. R. K. F.

Acid Treatment of Heterocyclic Imide and Iminazole Dyes to form them into a Very Finely Divided and Uniform State. J. F. Cullinan, L. D. Lytle, and American Cyanamid Co. *U.S.P.* 2,473,015.

Naphthoylene - (1:8:4:5) - bisiminazoles and perylene - 3:4:9:10-tetracarboxydiimides are made into a slurry with 20–40 parts of sulphuric acid per part of dye. The amount and concentration of acid are such that at the reaction temperature not > 10% of the dye is in solution at any one time. The slurry is agitated until the dye is converted completely to the insoluble sulphate, which is then hydrolysed to obtain the finely divided dye in particles of uniform size. The products are particularly suitable for use in pigment padding or in printing. C. O. C.

Quinoneimine Dyes from Hydroxybenzamidobenzaldehyde and Hydroxybenzsulphonamidobenzaldehyde Acetals of Lower Alkanols and 1:2- and 1:3-Alkanediols. E. L. Martin and Du Pont. *U.S.P.* 2,472,911.

Dyes of general formula—



or

(R^1 = alkyl of 1–4 C; R^2, R^3, R^4 = H, halogen, or short-chain hydrocarbon radicals of 1–4 C; X = SO_2 or CO; Y^1 and Y^2 = separately the alkyl portion of an alkoxy group of 1–4 C and together may be joined to form a bivalent sat. aliphatic hydrocarbon radical of 2–4 C wherein 2–3 atoms only are in the chain between the two O atoms) can be prepared by reaction of a lower acetal with a *p*-aminodialkylaniline in presence of a mild oxidising agent under alkaline conditions. They dye cotton, wool, silk, or nylon very bright blues to greens when applied from a mildly alkaline hydrosulphite vat and then oxidised with sodium dichromate or perborate. The dyeings have exceptionally good wet fastness on all four fibres. They are also useful in colour photography. C. O. C.

Blue to Green Vanadium–Zirconium–Silica Pigments. Harshaw Chemical Co. *B.P.* 625,448.

Complex Calcium Carbonate–Silicate Pigment for use with Rubber. H. F. Roderick, F. M. Zorn, and Wyandotte Chemicals Corpn. *U.S.P.* 2,470,577.

Metal Powders produced by Electrolytic Reduction. E. H. E. Johansson. *B.P.* 626,636.

Metallic Powders. S. K. Wellman Co. *B.P.* 628,183.

Beads or Pellets of Furnace Black. Columbian Carbon Co. and C. W. Schweitzer. *B.P.* 624,914.

Readily handled pellets of furnace black are obtained by uniformly heating preformed pellets containing furnace black and not < 0·1% of acetone-extractable matter in a static atmosphere at 1000–2000°F. for a period of time insufficient to change the character of the black or to cause substantial loss of constituents and finally cooling in a static atmosphere. C. O. C.

Dustless Carbon Black. C. M. Blow. *B.P.* 625,872.

Carbon Black. Phillips Petroleum Co. *B.P.* 627,872.

Printing of Nylon. General Aniline & Film Corpn., H. H. Bestehorn, and H. W. Grimmel. (IX, p. 85.)

V— PAINTS; ENAMELS; INKS

Flake Metal Powders and Paint. H. W. Greenwood. *Paint*, **19**, 301 (1949).

The so-called bronze or gold powders are mostly made from brass containing 5–15% zinc. The metal is finely divided and then treated in eddy, hammer, or ball mills until it is reduced to particles 0·000001–0·0002 in. thick and 10–15 times as long and broad. This procedure is also used for other metals, particularly aluminium. Several metal-flake powders are produced electrolytically. The largest single use for metal powders is now in paint. Bright zinc flake is now produced commercially in the U.S.A. and is particularly suitable for application in an alkyd resin vehicle. A similar product has been produced in Germany by stamping zinc with calcium metal and then heating for > 24 hr. at 40–50°c. to dry and roughen the powder; brass and copper powders have been produced in the same way. Stainless steel flake made from 18–8 stainless steel (18% chromium, 8% nickel) is also being produced commercially in the U.S.A., and gives silver-grey coatings with the characteristic bluish hue of stainless steel; in addition to its use in paints it can be used for coating paper. Flake nickel powder is produced electrolytically by the process of *U.S.P.* 2,365,356. Flake silver powder is produced by electrodepositing silver on stainless steel balls, flaking it off, and then mildly ball-milling it. The same process can be used for other metals. Flake silver powder in a cellulose nitrate vehicle is used for painting ceramics. C. O. C.

Pigment Properties of Titanium Dioxide. A. V. Pamfilov and S. V. Peltikhin. *J. Appl. Chem.* (*U.S.S.R.*), **22**, 245–249 (March 1949).

Pearl Essence. H. Mattin. *Ind. Finishing*, **25**, (7), 60, 62, 66, 68 (1949): *Chem. Abs.*, **43**, 5970 (1949).

Pearl essence is an 11% suspension in lacquer of guanine crystals from herring scales. The lacquer used is a 20–30-sec. cellulose nitrate solution in amyl or butyl acetate. C. O. C.

PATENTS

Paints with a Portland Cement Base. Devoe & Raynolds Co. Inc., C. R. Nelson, and R. E. Madison. *B.P.* 624,671.

Fungicidal Lacquer. W. S. Osborne. *U.S.P.* 2,472,847.
A fungicidal lacquer suitable for application to textiles, leather, wood, metals, or plastics comprises a clear melamine lacquer containing 2·2% by weight on the solids in the lacquer of a mixture of *o*-tolylazodiaminobenzene hydrochloride (8 parts) and tetrabromo-*o*-cresol (2).
C. O. C.

Wrinkle-drying Coating Composition. E. Lorenzo-Luaces. *B.P.* 626,696.
A wrinkle-drying coating composition consists of wrinkling or conjugate-double-bonded oil (100 parts by weight), an acrylic, melamine, or urea–formaldehyde resin (50) together with a solvent for the resin, and a 2 : 1 pigment–wrinkling oil paste (40–80). It is applicable to paper, fabric, or similar materials. C. O. C.

Coating Composition. Du Pont. *B.P.* 622,978.
A stable coating composition comprises an organic film-forming vehicle containing a water-insoluble cellulose ester or ether and, as pigment, hydrous iron oxide of average particle diameter < 100 mμ, and consisting of 0·2–5·0% of ferrous iron and 99·8–95% of ferric iron. It gives films of a strikingly beautiful transparency and of great resistance to weathering. Metallic powders, e.g. aluminium powder, may be incorporated without difficulty to provide a brilliancy not heretofore obtainable in greys.
C. O. C.

Powdered Resin–Pigment Compositions. Sherwin–Williams Co., W. T. Walton, and A. B. Holton. *B.P.* 626,695.
Powdered resin–pigment compositions, which form coating compositions when stirred into a liquid vehicle or can be used for shading coating compositions, are obtained by mixing a soluble resin which is non-softening at normal temperatures, a pigment, and 5–10% on the weight of the pigmented resin of an anti-bonding agent, e.g. mica, under conditions of shear and at such a temperature that the resin can undergo plastic flow, and then grinding to 40–200 mesh per linear inch. The proportion of resin to pigment varies from 9 : 1 to 2 : 8 as the average size of the pigment particles increases from 0·1 to 0·5 μ.
C. O. C.

Coating Compositions using Polyethylene-coated Metallic Pigments. B. C. Pratt and Du Pont. *U.S.P.* 2,472,680.

Pigment Coating Compositions exhibiting Resistance to Pigment Flotation. C. M. Sage and General Electric Co. *U.S.P.* 2,467,858.
Addition to pigmented resinous coating compositions of 0·000001–0·01% by weight of the hydrolysate of a compound of general formula $X{\cdot}Si(CH_3)_2{\cdot}CH_2{\cdot}Si(CH_3)_2{\cdot}X$, e.g. bis-(dimethylchlorosilyl)-methane, greatly reduces any tendency toward pigment flotation. C. O. C.

Enamelling. General Motors Corpn. and W. H. Pfeifer. *B.P.* 624,967.

Heat-drying Printing Ink. Curtis Publishing Co. *B.P.* 628,109.

Water-base Printing Ink. V. A. Lauderman and Champion Paper & Fibre Co. *U.S.P.* 2,468,633.

Water-setting Printing Inks. C. A. Rietz, R. F. Lecture, and Interchemical Corpn. *U.S.P.* 2,468,779.

Water-setting Printing Inks. C. A. Rietz and Interchemical Corpn. *U.S.P.* 2,472,125.

Impregnating Composition for Typewriter Ribbons for Direct Use on Cellulose-base Planographic Printing Plates. Addressograph-Multigraph Corpn. *B.P.* 628,444.

White Writing Ink. W. E. Decker and Technical Specialities Co. *U.S.P.* 2,460,925.

VI—FIBRES; YARNS; FABRICS

Developments in Fibres, Dyes, and Chemical Processing of Textiles. K. Brass. *Kolloid-Z.*, 113, 110–120 (May 1949).
A review of the literature regarding modern developments in the treatment of cellulosic fibres. Properties of cotton; attack by micro-organisms and its prevention; kier boiling and bleaching; mercerising; scouring, soaps, and auxiliary products; theories of dyeing; dyeing methods; dyes; finishing; printing. Properties and treatment of bast fibres (flax, hemp, ramie, and jute). B. K.

Acidity of Cellulose. A. J. A. van der Wyk and M. Studer. *Helv. Chim. Acta*, 32, 1698–1712 (Aug. 1949).
By taking account of the Donnan effect it is possible to titrate insoluble acids, and theory indicates that an excess of a strong electrolyte is essential during this titration. The analysis of the titration curves obtained with purified celluloses, whether native or regenerated from their cupra-ammoniacal solutions, enables the dissociation constants to be calculated. The latter are somewhat analogous to the constants of monobasic acids, but are much smaller than those of hydroxy acids. It is concluded that pure celluloses have no COOH groups, and the acidic character is ascribed to the accumulation of OH groups. H. H. H.

Structure and Polymolecularity of Cellulose. T. Svedberg. *Svensk Papperstidning*, 52, 157–164 (15th April 1949).
Frequency curves of cellulose were studied by means of fractional precipitation, ultracentrifugal sedimentation, and the osmotic balance, using the nitrates. The fractions are summed up as triangles with their widths as measured in the ultracentrifuge, and the resulting frequency curves are rather complicated functions generally containing several maxima. Native and depolymerised celluloses (sulphite and sulphate pulps, rayon, etc.) all have a common maximum for degrees of polymerisation (D.P.) of 70–100. After strong degradation most of the cellulose accumulates at D.P. 100 and 200. Only the first of these maxima is left after boiling in 2·5 N. sulphuric acid. Earlier investigations showed cellulose to be fibrillar and partly crystalline. Degradation experiments by hydrolysis and ultrasonic waves were carried out as well as electron microscopy, and electron and X-ray diffraction studies. Aqueous colloidal solutions of cellulose were prepared, having rod-like cellulose particles of fairly uniform dimensions (length approx. 500 A., width 50–100 A.). They give sharp electron diffraction patterns indicating good crystallisation, and their length corresponds to that of cellulose molecules in the first maximum of the frequency curves. It is probable that the isolated particles are the crystalline parts (crystallites) of the cellulose fibrils, earlier postulated as micelles in the fibres from X-ray investigations. The micelles isolated by hydrolysis give the same Debye–Scherrer diffraction lines as native cellulose, but the pattern is sharper and of higher intensity, indicating that the amorphous phase of the cellulose was eliminated by the hydrolysis. S. V. S.

Investigation on Cellulose Reactions. VII—The Periodate Method for estimating the amount of easily Accessible Materials in Cellulose. T. Timell, *Svensk Papperstidning*, 52, 107–112 (15th March 1949).
The chemical methods hitherto used for estimating the amount of amorphous or easily accessible material in cellulose are briefly discussed. A comparison of the values obtained with a number of cellulose samples by Mark's periodate method with those found by other means confirm the usefulness of the periodate method in characterising various celluloses. By methylation of sodium cupricellulose and periodic acid oxidation of the methyl celluloses thus obtained, it is shown that the amorphous portion is first converted in the formation of cellulose ethers. Nickerson's method was found to give the same result as the periodate method. S. V. S.

Mechanism of the Hydrolysis of Cellulose—I. V. I. Sharkov, V. S. Muromtsev, and G. D. Paramonova. *J. Appl. Chem.* (*U.S.S.R.*), 21, 1037–1044 (Oct. 1948).
Measurements were made of the rate of hydrolysis of cellulose by acid. A readily hydrolysable fraction was found which comprised 2·45% for cotton cellulose, and 2·84% for sulphite cellulose from fir. The rate of hydrolysis of the residue was practically the same for both types of cellulose. Cotton cellulose and viscose rayon after oxidation to polyuronic acids by Kenyon's method were found to undergo hydrolysis at the same rate as the original material. It is concluded that the varying rates of hydrolysis found in cellulose preparations are to be interpreted in terms of varying accessibility of the macromolecule to the hydrolysing agent, and not to the presence of uronic acid or xylose units. A. E. S.

Mechanism of the Hydrolysis of Cellulose—II. V. I. Sharkov, G. D. Paramonova, and M. N. Klikasheva. *J. Appl. Chem.* (*U.S.S.R.*), **21**, 1073–1082 (Oct. 1948).

Cellulose, hydrocellulose, and viscose fibre, all prepared from wood and dried at 20°c., are hydrolysed by acid appreciably more slowly than the same preparations dried at 90–105°c. Hydrocellulose dried at 20°c. and then heated at 105°c. retains its low activity. When hydrocellulose is prepared with the loss of the readily hydrolysable fraction referred to in part I, it is found that after drying, this fraction is partly re-established. After mercerisation, sulphite cellulose and hydrocellulose derived from it are much more readily hydrolysed. The reactivity of viscose rayon is, however, reduced by mercerisation. A. E. S.

Origin of Hygroscopicity of Jute. P. H. Hermans and M. K. Sen. *Nature*, **164**, 628–629 (8th Oct. 1949).

The greater hygroscopicity of jute as compared with other natural fibres is ascribed almost wholly to the presence of polyuronides, xylan, and hexosan. Lignin contributes inappreciably to its hygroscopicity. The view is quantitatively consistent with the known constituents of jute and the assumption that 30% of the α-cellulose is amorphous, as in all the purer native fibres. W. J. M.

Ramie Production in Florida. ORR 73/49* (PB 97,342).

A progress report (196 pp.) prepared by the U.S. Department of Agriculture and the University of Florida Agricultural Experiment Stations, Everglades branch. It gives the results of recent studies on ramie culture and the production of fibres from it, including a detailed review of degumming methods and equipment. There are outstanding differences between the cross-sections of several of the varieties of ramie. C. O. C.

* Photocopies available from T.I.D.U., Board of Trade, 40 Cadogan Square, London S.W.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.—see J.S.D.C., **66**, 53 (Jan. 1950).

Ion Exchange and Fibre Contraction. I. MacArthur, J. L. Mongar, and A. Wassermann. *Nature*, **164**, 110–111 (16th July 1949).

Further evidence is given that the reason for the contraction of swollen calcium alginate fibres when placed in sodium chloride solutions is ion exchange and not osmotic "deswelling". This is based on the following experimental evidence— weight changes in the fibre during the treatment, the anisotropic changes involved, chemical analysis, X-ray studies, and finally the analogy in the behaviour to keratin, collagen, and other long-chain compounds. W. J. M.

Action of Strong and Weak Acids on Wool, Silk, and Polyamides. E. Elöd and H. G. Fröhlich. *Melliand Textilber.*, **30**, 239–243 (June 1949).

After reviewing published work on the subject, the results of investigation by the authors are given. Relationship between acid-binding power of wool and silk, concentration of hydrochloric acid, and reaction time. Effect of pH on the absorption of weak acids by wool, silk, and nylon. Comparison of the absorption of strong and weak acids by wool, silk, and nylon at equivalent concentrations. B. K.

Is the Adsorption of Water Vapour by Wool Photosensitive? C. Camposortega, F. Moncada, and J. W. Rowen. *J.S.C.I.*, **68**, 118–119 (April 1949).

It has been reported that light has a reversible action on the adsorption of water vapour by wool. An attempt to measure this was made unsuccessfully, even with a light intensity greater than originally reported, and it is concluded that the phenomenon is very difficult to reproduce or does not exist. W. J. M.

Photosensitive Adsorption of Water Vapour on Wool—II. N. F. H. Bright and T. Carson. *J.S.C.I.*, **67**, 463–464 (Dec. 1948).

Further experimental work on the photosensitivity of the adsorption of water vapour on wool at 5–20% R.H. has shown that the effect is not reproducible. On one batch of material, within the critical R.H. range, increase in illumination caused an increase in regain for a sample conditioned on the adsorption isotherm (the reverse not being true for a decrease in illumination), whereas a decrease in illumination caused a decrease in regain for a sample conditioned on the desorption isotherm (again the reverse not being true for an increase in illumination). Workers at the Wool Industries Research Association, Leeds, were unable to reproduce the effect, and subsequently the authors were also unable to repeat their original findings. Alternative explanations of the phenomenon are considered. G. L.

Influence of Fine Structure on the Properties of Cellulose Hydrate Fibres. E. Elöd. *Textil-Rund.*, **4**, 117–126 (April 1949).

The differences between the fine structure of natural and hydrated cellulose fibres are discussed with particular reference to the cause of the increased water absorption and consequent lower wet strength of the cellulose hydrate fibres. Measurements on a large number of cellulose fibres show the close relation between density and swelling, the swelling decreasing with increasing density. The density of ordinary viscose rayon is about 1·51, whereas that of cotton is about 1·53. Improvements in the wet strength of rayon may therefore be effected by increasing its density. It was found possible to prepare rayon with a density of 1·524 whose water absorption was 60% instead of about 100%, which is the usual figure for viscose rayon. It has been reported that the density of rayons is not uniform but that the core of the fibre is surrounded by a skin of higher density. It was not possible to confirm this in a convincing manner by the usual method of staining fibre sections. A new technique for the investigation of density variation across the fibre sections was elaborated on the basis of the observation that the fibres can be topochemically acetylated by means of acetic anhydride in an indifferent solvent such as benzene or toluene. Staining with acetate-rayon dyes shows that the acetylation proceeds from the surface of the fibre inwards, so that an increasing thickness of the outer layer can be acetylated and then removed by dissolving in a mixture of chloroform and methanol. With rayons spun in the usual acid salt bath, progressive removal of the outer layer of the fibres leads to an increase in the swelling of the fibres, whilst their density decreases. The results do not indicate a well defined skin but rather a gradual change in properties. Lanusa-type and Cuprama rayons do not give this result but may show a slight decrease in swelling as their surface is removed. Measurements of swelling anisotropy, on fibres whose diameter had been progressively decreased in the manner described, confirm that the outer layers of ordinary viscose fibres are more closely packed than the core, but that the reverse is true for Lanusa and Cuprama rayons. F. A.

X-ray Investigations on the Stretching Mechanism and Fine Structure of Artificial Cellulose Fibres. W. Kart and A. Prietzschk. *Kolloid Z.*, **114**, 23–35 (July 1949).

A detailed description with 13 diagrams is given of X-ray data with respect to cuprammonium and viscose rayon, whereby changes during stretching are followed and conclusions with respect to its mechanism derived, the latter being based on the orientation parameters of the crystallites. H. H. H.

Structural Viscosity of Viscose. P. Herrent, F. Mouraux, and A. Lude. *Research*, **2**, 486–492 (Oct. 1949).

That point in the ripening of viscose which experience has shown is the optimum moment in spinning is marked by two independent phenomena. The first is that, if the variation of relative viscosity for a constant increase of shear is plotted as a function of the ripeness index, then the slope of the resulting curve decreases as the Mottenroth ripeness index decreases, passes through a sharp turning point, and then decreases. The same happens with the e.m.f. developed by a silver–silver nitrate concentration cell set up in ripening viscose, there being a very sharp minimum at the moment of precipitation of the silver xanthate. These two effects are directly due to the nature, shape, and size of the particles in the solution. These effects are probably purely chemical in nature and may mark a moment of balance in a sequence of possible reactions. C. O. C.

Chemistry of Viscose and the Xanthates. V— Thioanhydrides of Xanthic Acids and their Reactions. S. N. Danilov, N. M. Grad, and V. O. Klesman. *J. Appl. Chem.* (*U.S.S.R.*), **22**, 625–633 (June 1949).

The lower xanthic thioanhydrides are attacked by

alcoholic caustic alkali and alcoholic ammonia with the formation of xanthates. The thioanhydride of cellulose xanthate is attacked also by *aqueous* caustic soda and ammonia with the formation of sodium or ammonium cellulose xanthate, cellulose, and carbonyl sulphide. Aniline reacts to form a xanthanilide containing the group $-O\cdot CS\cdot NH\cdot C_6H_5$. A. E. S.

Viscose Rayon Fibres. II— Orientation of Skin and Core. J. M. Preston and K. I. Narasimhan. *J. Textile Inst.*, **40**, T 327–T 337 (May 1949).

The double refractions of the skin and core of three series of viscose fibres have been measured. It was found in all cases except one, in which the fibre was nearly isotropic, that the double refraction of the skin was greater than that of the core, and that the difference in double refraction was symbatic with the double refraction of the skin. The theory is proposed that the skin crystalline structure is partly planar and is radially oriented. On this basis the appropriate double refractions were calculated. The experimental values were found to lie close to the straight-line plot of the theoretical figures. W. J. M.

Cuprammonium Solutions of Cellulose. I— Effect of Ammonia and Alcohol on the Optical Rotation of Cuprammonium Solutions of Cellulose. M. I. Arkhipov and V. P. Kharitonova. *J. Appl. Chem. (U.S.S.R.)*, **22**, 761–770 (July 1949).

Determinations are made of the optical rotation of solutions of cellulose in cuprammonium hydroxide solutions of varied composition. It is found that when the ammonia content is increased from a low value in solutions containing copper and cellulose at low concentration, the laevorotation at first diminishes to a minimum value and then rises. In solutions containing higher amounts of copper and cellulose the rotation rises continuously as the concentration of ammonia is increased. The addition of alcohol also increases the rotation. It is considered that the optical activity of these solutions is directly related to the extent of the association between cellulose and copper, and that this is increased by a reduction in the degree of dissociation of the cuprammonium bases present and also by the presence of colloidal copper hydroxide, which, at low concentrations of copper, ammonia, and cellulose, is present in relatively large amounts. Addition of ammonia then leads, in the first place, to a diminution in the concentration of the copper hydroxide and a corresponding fall in the optical rotation; with further additions the reduction in the dissociation of the cuprammonium bases becomes significant, and the optical rotation rises. In more concentrated solutions the first effect is of less importance, and the optical rotation rises continuously with the addition of ammonia, caustic soda, alcohol, or other agent capable of reducing the degree of dissociation of the cuprammonium bases. The experimental results cannot be explained in terms of a displacement of part of the copper from a complex cation to a copper–cellulose anion, as supposed by Hess and Traube in explaining the effect of additions of caustic soda to cuprammonium solutions of cellulose. Nor can the fact that, in a cuprammonium solvent, any excess of undissolved or colloidal copper hydroxide may go into solution when cellulose is added, be explained, following Hess and Traube, as the result of the liberation of ammonia; it is to be attributed to the removal of part of the copper from the sphere of equilibrium, forming a copper–cellulose compound.

Experiments with cuprammonium solutions of sucrose are also described and discussed. A. E. S.

Regenerated Keratin Fibres. R. L. Wormell and F. Happey. *Nature*, **163**, 18 (1st Jan. 1949).

Keratin has been dissolved in cuprammonium solution and spun. The X-ray photographs show that the keratin is in the denatured β-keratin form, the folded α form having been destroyed; however, fibres with a tenacity of 0·8 g. per denier have been prepared, which brings it into the usable textile range. W. J. M.

Regenerated Keratin Fibres. E. H. Mercer. *Nature*, **163**, 18–19 (1st Jan. 1949).

Two kinds of precipitated protein have been obtained by salting out keratin dissolved in saturated urea with reducing agents. These are— (*a*) at pH 6–7 and 40°C. a non-orientable fibrous protein giving a diffuse X-ray pattern, and (*b*) at pH 8–9 and 50°C. an orientable fibrous form with the typical α-type X-ray pattern. W. J. M.

Structures of α-Keratin and Synthetic Polypeptides. W. T. Astbury. *Nature*, **164**, 439–440 (10th Sept. 1949).

Earlier results and conclusions from the study of the keratin–myosin–epidermis–fibrinogen group of fibrous proteins are assembled to show why the author and his colleagues are not yet able to adopt the α-diagram or the correctness of the intramolecular fold put forward to explain it. These are— (1) the formidable objection on X-ray grounds; (2) it is not sufficient to account for an extension of 35–40%, when it is known that not only keratin fibres but also oriented myosin can show reversible elasticity up to extensions of $\sim$ 100%; (3) detailed examination and measurement of the diagram given by certain synthetic polypeptides show that there are important differences between these and the α-keratin group diagrams; (4) the suggestions of Brown *et al.* (*Nature*, **163**, 834 (1949)) are untenable; (5) poly-DL-phenylalanine has been obtained in two forms, one of which gives a β-diagram; and (6) the infra-red situation is not yet diagnostic. H. H. H.

Softening Temperatures of various Fibrous Keratins. H. Zahn. *Kolloid-Z.*, **113**, 157–159 (June 1949).

The contraction of various keratin fibres in 50% aqueous phenol in relation to the temperature has been examined. The temperature necessary to bring about average contraction of the fibres (softening temperature) depends on the type of fibre. Typical temperatures are 84°C. for wool and 95°C. for human hair. The relationships between the softening temperature, cystine content, and the histological structure of the fibres are discussed. B. K.

Further Studies in Synthetic Polypeptides. C. J. Brown, D. Coleman, and A. C. Farthing. *Nature*, **163**, 834–835 (28th May 1949).

The results of Astbury and Dalgliesh (*Nature*, **162**, 596 (1948)), that the majority of the synthetic polypeptides so far prepared give X-ray powder photographs resembling those given by β-proteins, have been confirmed, but the copolymers (1:1 mol.) of DL-β-phenylalanine, L-leucine, and α-amino-*iso*butyric acid give X-ray powder photographs the two principal diffraction rings of which correspond to interplanar spacings of 5·2 and 11·7 A. Films from these copolymers give an oriented diffraction pattern very similar to those of α-proteins. The similarity of the photographs of the synthetic fibres to that of natural keratin leads to some interesting suggestions regarding their structure. H. H. H.

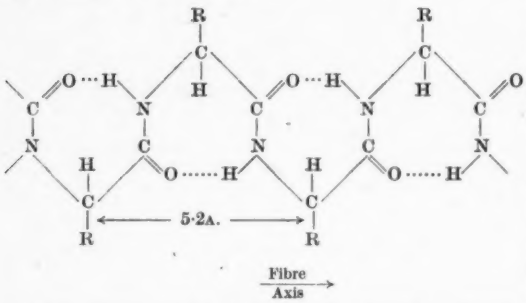
New Evidence on the Structure of some Proteins from Measurements with Polarised Infra-red Radiation. E. J. Ambrose, A. Elliott, and R. B. Temple. *Nature*, **163**, 859–862 (4th June 1949).

In oriented (rolled) polyglutamic ester and in keratin obtained from porcupine quill, the preferred direction of the N–H bonds is shown by polarised infra-red measurements to be parallel to the chain orientation. This strongly supports the view of Ambrose and Hanby (*Nature*, **163**, 483 (1949)) that the backbone or chain is folded to form a 7-membered ring. In view of the importance of the interpretation of the α-structure, several proteins of the keratin–myosin group have been examined, with results all in harmony with those obtained in the first instance with polyglutamic ester and α-keratin. The spectra were recorded in the 3-μ. region with a lithium fluoride spectrometer equipped with a selenium transmission polariser. The main features of all the spectra are the bands due to stretching frequencies of the C–H bonds at $\sim$ 2900 cm.$^{-1}$, and two bands which almost certainly arise from N–H stretching modes, a strong band at $\sim$ 3310 cm.$^{-1}$ and a much weaker one at $\sim$ 3060 cm.$^{-1}$. Both N–H bands show parallel dichroism in myosin, tropomyosin, and α-keratin, but are markedly perpendicular in feather keratin, which occurs naturally in the β-form. These facts can be interpreted on the assumption that the polypeptide chains are folded in the α-form and extended in the β-form. The paper concludes with speculations on the macroscopic properties of proteins. H. H. H.

Evidence for α-Protein Structure in Polypeptides. C. H. Bamford, W. E. Hanby, and F. Happey. *Nature*, **164**, 138–139 (23rd July 1949).

A preliminary review is given of the X-ray examination of a copolymer of γ-methyl L-glutamate with DL-β-

phenylalanine and poly-DL-β-phenylalanine. The diagrams show that both polymers have very similar structures, and, provisionally, unit cells (or submultiples) for each are suggested. The resemblance of these polypeptides to α-protein in respect to the repeat along the fibre axis can clearly be seen, and there is no evidence of a β- or cross-β-structure. The repeat distance along the fibre axis is in agreement with the structure—



and it is unnecessary to postulate the abnormal backbone spacing given by Astbury *et al.* (*Nature*, **162**, 596 (1948)). Although these fibres have been oriented by stretching, it has not been possible to extend them into a β-configuration. The results of the recent X-ray study of the copolymer of L-leucine and DL-β-phenylalanine by Brown *et al.* (*Nature*, **163**, 834 (1949)) can be equally well explained by the above ideas, without assuming that the chains lie perpendicular to the fibre axis, and without postulating a backbone spacing. H. H. H.

Vicara— New Fiber derived from Zein. W. P. ter Horst. *Amer. Dyestuff Rep.*, **38**, P335–P338 (18th April 1949).

Vicara is claimed to be the best man-made protein fibre yet invented. Its most striking advantages are its stability to acids, alkalis, and solvents and the cheapness of zein, from which it is prepared. It is more akin to wool than to the other fibres in normal production. It has good mechanical and chemical properties with a high dye uptake, is resistant to moth and mould attack, and may readily be handled by conventional cotton and woollen systems. Clothing, upholstery, and novelty fabrics are the uses to which it is expected to be put. W. J. M.

Polyethylene Terephthalate and its Early Development. D. V. N. Hardy. *J.S.C.I.*, **67**, 426–432 (Nov. 1948).

The paper places on record experimental work carried out on the fibre-forming polyester, polyethylene terephthalate, at the Chemical Research Laboratory, Teddington (1942–1944). The polyester was prepared from ethylene glycol and methyl terephthalate by the method of Whinfield and Dickson (*B.P.* 578,079). The condensation was carried out in glass and in metal apparatus, both of which are described. Satisfactory filaments were not produced on extrusion of the melt under a high pressure of nitrogen, owing partly to degradation and partly to inclusion of bubbles produced on liberation of dissolved nitrogen. Filaments were prepared by extruding the polyester from a glass apparatus immediately after preparation and were cold-drawn. A number of physical properties are listed, including measurements of strength and extension. Maximum strength of the fibre was not attained in this early work. G. L.

Estimation of the Crystalline Portion of Macromolecular Synthetic Fibres. A. Sippel. *Kolloid-Z.*, 113, 74–82 (May 1949).

A theoretical method developed by the author for the estimation of the crystalline portion of macromolecular fibres has been described previously (*ibid.*, 112, 80 (Feb.–March 1949)). It has been applied experimentally to cellulose acetate fibres made by various methods, polyamide fibres, and fibres made from chlorinated polyvinyl chloride. The required relationship between tensile strength and degree of polymerisation has been confirmed, both in the case of degradation due to light exposure as well as with fibres from raw materials of varying degrees of polymerisation. Conclusions can be drawn regarding the molecular structure of the fibres, such as the arrangement of the crystallites. B. K.

Survey of Various Manufacturing Methods in Use by Worsted Industry for Production of Cloth, Serge, O.D. ORR 62/49* (PB 86,251).

A U.S. Govt. report on investigations into the factors causing deviations from specification of cloth deliveries. It deals with an analysis of the manufacturing processes used in producing O.D. 18-oz. worsted serge at 43 mills. It includes information on the various wool scouring, top-dyeing, and cloth-finishing processes used. Three basic factors existing in the worsted industry preclude the drawing of any specific conclusions or recommendation of preferred methods. These are (1) plant and machinery vary from mill to mill, (2) some mills are completely integrated and others only partly, and (3) geographical location of the mill is an important influence in the processing of textile fabrics. There is a brief supplementary report on the finishing methods used in some mills for 10½-oz. serges and flannels and for 18-oz. "elastique". C. O. C.

* Photocopies available from T.I.D.U., Board of Trade, 40 Cadogan Square, London S.W.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.—see J.S.D.C., **66**, 53 (Jan. 1950).

Textile Chemistry and Physiology. O. Mecheels. *Textil-Rund.*, **4**, 271–279 (Aug. 1949).

The physiological properties of textiles destined for clothing are discussed with special reference to heat retention, absorption of perspiration, and air porosity. Dyeing of wool with chrome dyes results in loss in heat retention and marked increase in air porosity. Neolans (Ciba) and other premetallised dyes have a low chrome content and behave in a similar manner to acid dyes, having little effect on heat retention or air porosity. An increase in resistance to bacteriological and fungicidal attack is brought about by dyeing with chrome dyes. Reference is made to the work carried out by the A.A.T.C.C. on the absorption of infra-red radiation of materials dyed with different groups of dyes. The aseptic properties of dyes in relation to their chemical constitution are discussed, as well as the influence of cloth construction on permeability to ultra-violet radiation. B. K.

Treating and Handling of Nylon Hosiery to Prevent Snagging during Manufacture. A. J. Olson. *Amer. Dyestuff Rep.*, **38**, P60–P61 (24th Jan. 1949).

Precautions to prevent snagging, which have been adopted as a result of experience at all stages of manufacture from yarn throwing to packing the finished hose, are described. Emphasis is placed on the use of a suitable water-soluble yarn size, the care of operatives' hands, and frequent inspection of boarding forms, etc. to ensure perfect smoothness. W. K. R.

PATENTS

Polyamides. J. Lincoln and J. G. N. Drewitt. *B.P.* 627,205.

Fibre-forming polyamides are obtained by treating a diprimary diamine, e.g. hexamethylenediamine, with equimol. proportions of a tricarboxylic acid having an imide-forming pair of carboxyl groups separated by three atoms and a carboxyl group separated from each of the others by a number of atoms other than 2, e.g. pentane-1:3:5-tricarboxylic acid. W. G. C.

Linear Polyesters. Wingfoot Corpn. *B.P.* 627,270.

Fibre-forming linear polyesters are obtained by heating a glycol having > 3 atoms between the hydroxyl groups with the chloride of a dibasic acid having > 3 atoms between the carboxyl groups until the polyester has an average mol. wt. $> 10{,}000$, e.g. decamethylene glycol and sebacyl chloride. W. G. C.

Polyamine-Triazole Condensates. J. W. Fisher and E. W. Wheatley. *B.P.* 627,124.

Linear polymers which can be cold-drawn to form filaments are produced by condensing 40–80% of a poly-1:2:4-triazole with 20–60% of a monomeric bifunctional amide-forming substance, e.g. hexamethylenediammonium adipate. W. G. C.

Coir Fibre— Structure and Identification of Damage. S. R. Sengupta, B. B. L. Saxena, and A. N. Mukerjee. (XIV, p. 99.)

VII—DESIZING; SCOURING; CARBONISING; BLEACHING

Modern Trends in Piecegoods Preparation, Dyeing, and Finishing. C. N. Rabold. *Amer. Dyestuff Rep.*, 38, P67–P68, P77 (24th Jan. 1949).

Current practice in the continuous washing, bleaching, vat dyeing, and finishing of cotton piece goods is described. W. K. R.

Statistical Methods in Detergency Investigations. A. J. Feuell and R. E. Wagg. *Research*, 2, 334–337 (July 1949).

The statistical method of factorial experimentation has been applied to the study of the washing and suspending powers of a ternary system comprising a non-ionic detergent (Lissapol N (ICI)), sodium carbonate, and sodium carboxymethyl cellulose (Cellofas WFZ (ICI)). It is shown that high soil-removal power is not necessarily associated with a correspondingly high suspending power; that increase in concentration of soda ash enhances washing power but depresses suspending power, although both effects fall off at the highest concentration; and that the beneficial action of the Cellofas is attributable mainly to its suspending power. C. O. C.

Action of Cellulose Ethers when added to Scouring Agents. E. Bartholomé and K. Buschmann. *Melliand Textilber.*, 30, 249–253 (June 1949).

The addition of cellulose ethers, especially sodium salts of cellulose glycollic acid, improves the scouring efficiency of synthetic scouring agents, although the products themselves have no scouring action. The authors' experiments show that cellulose ethers have little action in the scouring bath, but are absorbed by the fibre and displace the dirt. B. K.

Data on a Laboratory Method for Wool Raw Stock Detergency. E. A. Leonard and L. Beck. *Amer. Dyestuff Rep.*, 38, P348–P352 (18th April 1949).

The continuous scouring of wool has been investigated by a laboratory method in which the process variables are controlled. The results are illustrated graphically, and it is shown that the temperature, type, and concentration of detergent and builder, immersion time, and squeeze roll pressures all have an important bearing on the scouring effectiveness. The method is low in cost, easily assembled, and highly flexible. W. J. M.

Action of Sodium Carbonate on Lime Soaps during Bleaching. P. Anglaret. *Teintex*, 13, 239–245 (July 1948).

Experiment has shown that a large excess of Na_2CO_3 is essential to convert calcium oleate into sodium oleate. The excess required varies inversely as the concentration of calcium oleate present. In the bleaching operation, where the quantities of lime soap present may be of the order of 1%, the quantities of Na_2CO_3 required to effect conversion would be so large as to render the process impracticable, and it is therefore necessary to mix suitable compounds (Trilon, etc.) with the soaps if loss of detergent value is to be avoided when calcareous water must be used. R. B. W.

Accelerated Bleach for Linen Fabrics. N. N. Kuzub and P. V. Moryganov. *Tekstil. Prom.*, 8, 30–32 (Nov. 1948).

The normal linen bleach, which occupies 7–10 days, is replaced by a process which takes only a few hours and is adapted to continuous running. The finished fabric has a higher fatty content and a lower absorbency, but this is not regarded as of great importance. It is of normal whiteness and is superior as regards strength, loss in weight during process, and cuprammonium viscosity. The recommended process is as follows—

(i) Treatment for 1 hr. at 100°c. in a bath containing 1 g. of sodium carbonate and up to 1 g. of sodium hydroxide per litre, followed by rinsing.

(ii) Boiling in lime and caustic soda at 100°c. for 1 hr.

(iii) Impregnation in dilute hydrochloric acid followed by treatment in a hypochlorite bath (3 g. of active chlorine per litre) at 18°c. for 30 min. Sour and rinse.

(iv) Further boiling in lime and caustic soda for 90 min. Sour and rinse.

(v) Treatment for 40 min. at 90°c. in a "spent" peroxide bath containing 0·5 g. of hydrogen peroxide per litre.

(vi) A two-bath peroxide bleach— impregnation in 3% hydrogen peroxide and squeeze to 70% uptake, followed by treatment for 40 min. at 90°c. in a bath containing per litre— 2 g. sodium carbonate, 7 g. sodium silicate, 1·2 g. caustic soda, and 2 g. soap. A. E. S.

PATENTS

Dispersing Moisture in a Dry Cleaning Solvent. C. S. Arnold and Emery Industries Inc. *U.S.P.* 2,471,667.

Moisture for removing water-soluble matter from the goods being processed is dispersed in a dry cleaning solvent by establishing turbulence at a local area in a confined moving stream of solvent and projecting atomised water into this area in the line of flow of the solvent by means of an air blast. Suitable apparatus is described. C. O. C.

Carbonising Wool containing Cellulose Ester or Ether Rayon. A. Crummett and A. Mellor. *B.P.* 626,801.

Cellulose ester or ether rayons are removed from wool by carbonising with gaseous hydrogen chloride at 80–100°c. in presence of a swelling agent for the rayon. Thus 6 cwt. of rags containing 50% wool, 25% acetate rayon, and 25% cellulose fibres are effectively carbonised by treating for 2–3 hr. at 80–100°c. with a mixture of 90 lb. of concentrated hydrochloric acid and 30 lb. of glacial acetic or 85% formic acid. C. O. C.

Carbonising Wool–Acetate Rayon Mixtures. G. C. Ward, R. U. Genazzani, and Celanese Corpn. of America. *U.S.P.* 2,472,238.

The material is treated in an aqueous solution containing 0·1–1·0% sodium hydroxide and 5–25% sodium sulphate so as to saponify the acetate rayon and is then carbonised; e.g. treat for 30 min. at 40°c. in an aqueous solution containing 0·6% sodium hydroxide and 20% sodium sulphate, then for 10 min. at 28°c. in 6% aqueous sulphuric acid; then dry and bake for 10 min. at 110°c., dust, neutralise, and rinse. C. O. C.

Bleaching Webs containing Ground Wood. Buffalo Electro-Chemical Co. Inc. *B.P.* 626,794.

Webs containing ground wood pulp are bleached by first reducing their water content to < 250% and then treating either or both faces with an alkaline aqueous solution containing a peroxide and a phosphate. For webs containing 70% unbleached sulphite and 30% ground wood pulp impregnation with 1% of hydrogen peroxide (27·5%) and 1% of trisodium phosphate, on the dry weight, gave considerably increased brightness. C. O. C.

Bleaching Cellulosic Material. Mathieson Alkali Works and H. N. Tatomer. *B.P.* 625,201.

In the multi-stage bleaching of paper or paper pulp, cotton linters, hemp, cellulosic rayon, etc., any degree of whiteness may be obtained without appreciable degradation of the cellulose by using a chlorine–chlorine dioxide water in the later stages of the bleaching. This liquor is prepared by passing a mixture of chlorine and chlorine dioxide into water so as to dissolve at least all the chlorine dioxide and to give a solution containing chlorine and chlorine dioxide in the ratios of 1 : 1 to 1 : 4. Any unabsorbed gases from the preparation of this liquor are scrubbed with make-up liquor for an earlier stage of the bleaching, the chlorine demand of such stage being thereby partly or completely met. C. O. C.

Detergent Action. O. C. Bacon and J. E. Smith. (XIV, p. 97.)

VIII—DYEING

Relationship between Constitution of Dyes and their Dyeing Behaviour. H. Gerstner. *Melliand Textilber.*, 30, 253–256, 302–306, and 372 (June–Aug. 1949).

A review of the literature covering 58 references to recent work on the relationship between the chemical constitution of dyes and their dyeing behaviour on various fibres. B. K.

Current Developments in Dyeing and Finishing. L. S. Thompson. *Amer. Dyestuff Rep.*, **38**, P6–8, P32 (10th Jan. 1949).

A general description of the more modern methods of dyeing and finishing is given under the following headings — desizing, bleaching, dyeing, stabilised finishes, and machinery. W. J. M.

Application of Fast Colours to Mercerised Cotton Hosiery. C. H. Asbury. *Amer. Dyestuff Rep.*, **38**, P58, P59, P76 (24th Jan. 1949).

The application of azoic and vat dyes to cotton hosiery is described; with the former, no particular difficulties are involved, but with vat dyes it is essential to dye at high temperatures to obtain satisfactory penetration of the heels, and it is advisable to select dyes which are least affected by high temperatures and which exhaust slowly. A recommended procedure for coarse-gauge hose is to add the dispersed dyes, 10% sodium hydroxide, and retarding and penetrating agents to the bath at 200°F. The dry hose are then added (liquor : goods ratio 15 : 1) and worked in the cooling bath for 25 min., when the temperature is adjusted to 190°F.; 10% sodium hydrosulphite is added slowly during 10 min., and dyeing continued for a further 5 min., and this is followed by overflow rinsing, oxidising, and soaping. With fine-gauge or tightly knitted hose, where penetration is even more difficult, 5% corn sugar, which causes partial reduction at high temperatures, is added along with the dye, and dyeing is continued for 15 min. after the addition of the sodium hydrosulphite. W. K. R.

Theory of the Dyeing Process. XIII— Dependence of the Absorption of Acid and Direct Cotton Dyes by Wool on the pH of the Bath. N. V. Sokolova. *J. Appl. Chem.* (*U.S.S.R.*), **21**, 966–975 (Sept. 1948).

The absorption of a group of acid and direct cotton dyes by wool is examined over the pH range 1–8 at 100°C. (time of dyeing 3 hr.), and at 20°C. (time of dyeing 2 months). It is confirmed that the saturation uptake of a molecularly dispersed dye at pH 3–4 is about 80 mg.-equiv. per 100 g. of wool, as required by the chemical theory of dyeing. Below pH 2 there is appreciable hydrolysis of the wool, leading to a still greater uptake. Above pH 3–4 the absorption generally falls off in the expected manner. A. E. S.

Theory of the Dyeing Process. XIV— Dyeing of Indigo Carmine on Wool in presence of Sulphuric Acid. E. A. Veller. *J. Appl. Chem.* (*U.S.S.R.*), **21**, 1147–1151 (Nov. 1948).

When wool is dyed with indigosulphonic acid in presence of sulphuric acid, both acids are absorbed by the fibre. In concentrated baths the fibre becomes saturated with respect to both of the acids, so that the total absorption is about 80 mg.-equiv. per 100 g. wool, as for other acids and dyes. This is contrary to the findings of Trotman (J.S.D.C., **50**, 65 (1934)), who found the total absorption to rise without limit. Trotman's results are attributed to incomplete removal of mechanically-absorbed acid in the washing process. A. E. S.

Influence of Chlorination on Wool Dyeing. H. Luttringhaus. *Amer. Dyestuff Rep.*, **37**, P464–P465, P471–P472 (12th July 1948).

Both acid and alkaline wet chlorination of wool is practised in the U.S.A. to render wool shrink-resistant. Unlevel treatments are more common with the acid chlorination, but the alkaline chlorination produces a yellowing of the wool. Level-dyeing acid dyes, milling dyes and chrome, metallised, vat, and soluble vat dyes can all be applied readily provided details of the shrink-proofing treatment are known and provided that the treatment itself is level. For maximum fastness to washing, vats and the leuco esters are recommended, although for most practical purposes satisfactory fastness can be achieved by the use of chrome, metallised, or milling dyes. H. K.

Problems in Dyeing Wool, Acetate, and Viscose Fabrics. Anon. *Canadian Textile J.*, **65**, 42 (1st Oct. 1948).

Attempts to dye a fabric containing 85% wool and 15% viscose rayon with which was accidentally blended acetate rayon, are described. A satisfactory navy blue with good rubbing fastness was obtained by a one-bath process. A. S. F.

Latest Developments in the Dyeing and Finishing of Synthetic Fibres. W. G. Helmus. *Amer. Dyestuff Rep.*, **38**, P62–P64, P84 (24th Jan. 1949).

Recent developments in the pretreatment, dyeing, and finishing of fabrics made from manufactured fibres, and in processing equipment, are described briefly. W. K. R.

Dyeing of Nylon with Logwood. H. R. Tisdale. *Rayon Text.*, **29**, 79–81 (July 1948).

The normal wool and cotton dyeing methods for dyeing with logwood are not suitable for nylon. Two methods are given— (I) To prepare the dyebath dissolve 6 lb. of unoxidised logwood crystals and 3 oz. of acetic acid (76%) in 100 gal. of water, sieve into a dyeing machine, and make up to required amount. The scoured nylon is entered at 120–140°F., raised to 200°F., and maintained there for 30–40 min. The nylon remains there for one hour, and is drained and washed off in cold water. Fixing is carried out in a bath containing 40 oz. of sodium dichromate and 3 oz. of acetic acid (76%) in 100 gal. The material is entered at 120–140°F., raised slowly to 200°F., and kept there for 20–30 min. It is removed, washed, soaped, and washed again. (II) The usual method for dyeing with hematine is to mordant with 1% of sodium dichromate and 1% of lactic acid, by entering, bringing to the boil, and boiling for one hour. Rinse free from chrome. Dye in a bath with liquor ratio 20–25 : 1 with 25% of hematine crystals and 5% of soap at 140°F. for 30 min., raise to the boil, and boil for a further hour, drain and wash with 5–10% of soap at 140°F. for 20 min. Modified processes are also described for dying mixtures of nylon with wool, viscose, or cotton. The penetration of dye by these two methods is good, as shown by photomicrographs. W. J. M.

Dyeing of Wool–Nylon Blends. G. T. Hug. *Amer. Dyestuff Rep.*, **38**, 661–662 (5th Sept. 1949).

The best solidity of shade combined with good fastness properties on wool–nylon blends is obtained with neutral-dyeing acid dyes. Level-dyeing acid dyes may be used for pale or medium shades, but they must be carefully selected, and incompatible combinations avoided. Chrome dyes offer the best fastness properties, but their use is limited owing to the difficulty with which they are chromed on nylon. The substantivity of nylon for all types of acid dyes is decreased by adding a long-chain alkyl sulphate to the dyebath, and such compounds should not be used indiscriminately for scouring. A. S. F.

Decomposition of Direct Dyes during the Dyeing of Union Materials. E. Skrutkowski and J. P. Niederhauser. *Teintex*, **13**, 313–317 (Sept. 1948).

When dyeing union (wool–cotton, wool–viscose) material with direct dyes, a change of shade is sometimes observed due to the decomposition of the dye. Investigation has proved this to be due to the action in the presence of the wool fibre of certain ingredients (chlorine, insoluble magnesium) in the water. The trouble can be overcome by adding 8–10% urea (calculated on the wt. of material) to the dyebath, as recommended in *U.S.P.* 2,282,724, or by the addition of an ammonium salt, but the use of the latter compounds renders the dyebath acid on boiling and causes the dye to dye the wool fibre in preference to the cotton. Change of shade due to insufficient desulphurisation of the viscose can be overcome by adding 0·5% of an oxidising agent (sodium perborate). R. B. W.

Dyeing of Perlon with Palatine Fast Dyes. K. Anacker. *Melliand Textilber.*, **30**, 256–258 (June 1949).

Palatine Fast (IG) dyes are of interest for dyeing 100% Perlon, giving better fastness than Celliton (IG) dyes. They level well, but individual members of the range differ as regards exhaustion and compatibility. Many are suitable for dyeing unions of Perlon and wool in solid shades. B. K.

Dyeing of Rhofil. A. M. Baron. *Teintex*, **14**, 181–191 (May 1949).

Rhofil (Rhodiaceta) is polyvinyl chloride fibre in stretched filament form. It is thermoplastic and contracts at 68–70°C. Dyeing is carried out with dispersed acetate dyes, and good results have been obtained with Acetoquinone Yellow 4J, Acetoquinone Orange 4R, and Celliton Discharge Blue 2RF. These are all azo dyes, and this group is apparently preferable to anthraquinone dyes.

Two methods have been developed for the application of dispersed acetate dyes— (1) The scoured cloth is padded through a suspension of a suitable dye, squeezed, dried at a moderate temperature, and passed into a vaporisation chamber containing a volatile swelling agent such as ethyl acetate, methylene chloride, trichloroethylene, etc. at about 30°c. After development in the vaporisation chamber, the material is aired, washed off, and soaped to remove excess dye. (2) The scoured and dry cloth is padded through an emulsion of suitable dispersed acetate dyes emulsified with Solvent F, given one or two nips between rollers, wound on a cylinder, and allowed to lie for 2 hr., during which period the cylinder is given an occasional turn. The cloth is then wound off, dried at a moderate temperature, and soaped. Rhofil can also be dyed with azoic dyes by treatment at 60°c. in a bath containing both base and β-naphthol in alkaline solution, followed by development in sodium nitrite and hydrochloric acid at 60°c. B. K.

Practical Observations on the Protective Action of Sodium Pyrophosphate in Dyeing. P. Weyrich. *Melliand Textilber.*, **29**, 68 (Feb. 1948).

Following a paper by P. Rabe (*ibid.*, **28**, 352 (October 1947)), which describes the protective action of sodium pyrophosphate when dyeing in the presence of iron, the present paper gives the results of practical experience in the dyeing of cotton, wool, and staple fibre, which confirms the usefulness of an addition of pyrophosphate in practice. F. A.

Some Phases of High Temperature Dyeing. American Association of Textile Chemists and Colorists, Philadelphia Section. *Amer. Dyestuff Rep.*, **38**, P9–P32 (10th Jan. 1949).

High-temperature dyeings were carried out in a closed system under pressure. Stability tests were made on all the dyes and fibres used. On viscose rayon and cotton, direct dyes were found to give better levelling and, on cotton only, sulphur dyes gave stronger colours; on the other hand, the results with vat dyes were definitely inferior. Acid and direct dyes gave negligible coloration on cellulose acetate. The results with nylon indicated increased rate of diffusion and better covering of irregularities. On the other hand, the tenacity was reduced in the presence of strong acids, alkalis, soaps, and some detergents. Marking off, saturation values of direct and acid dyes, and fastness properties did not appear to be significantly affected. The results with wool indicated that the increased speed of dyeing allowed better diffusion inside the fibre, decrease in fibre selectivity, and with proper equipment would allow a tenfold increase in production without impairing either the fastness properties of the dyeing or the physical properties of the wool. W. J. M.

Protective Colloids in Vat Dyeing. P. Wengraf. *Textil-Rund.*, **4**, 328–332 (Sept. 1949).

Protective colloids of the Peregal O (IG) type bring about aggregation of the leuco vat dye molecules in the dyebath, and as a result the rate of absorption of the dye is reduced and a more level dyeing produced. A new method of assessing the protective action of colloids is proposed in which the quantity of an oxidising agent (sodium perborate or hydrogen peroxide) necessary to oxidise Cibanone Yellow dye vats (with and without the addition of colloid) is ascertained, and the ratio between the two figures gives an assessment of the protective action of the colloid. B. K.

PATENTS

Colouring Organic Derivatives of Cellulose. British Celanese Ltd. *B.P.* 626,740.

Modification of *B.P.* 583,349 (cf. J.S.D.C., **63**, 196 (1947)) The material is impregnated first with a dye dissolved in an aqueous monohydric alcohol containing 1–5 C and then with an aqueous inorganic swelling agent. Thus acetate rayon fabric is pad-dyed with a solution consisting of Alizarin Cyanine Green GHW (*C. I.* 1078) (2 parts by weight) in 70% aqueous ethyl alcohol (100). The bath is at 30°c., and the fabric passes through at 25 yd./min. with an immersion of 3 sec., and the nip such that the fabric retains 70% of its weight of the liquor. It then passes directly into a 20% aqueous solution of sodium thiocyanate at 30°c., then through the nip of a padding mangle to a rinsing bath. A level, well penetrated green dyeing is obtained. C. O. C.

Pigment-colouring Textiles. Du Pont, M. O. Shows, and P. L. Meunier. *B.P.* 626,581.

Textiles are dyed or printed with a composition made up of a volatile liquid vehicle, a pigment, and as a binder a film-forming linear polyamide some of whose amide N atoms bear a side-chain of general formula $-CH_2\cdot OR$ (OR = the radical of a saturated or unsaturated aliphatic, aromatic, or carboxy-substituted aliphatic or aromatic alcohol), and then heated to evaporate the liquid vehicle and insolubilise the binder. Thus, all parts being by weight, *N*-methoxymethylpolyhexamethyleneadipamide was dissolved in a 70–30 methanol–water mixture (90) at 50°c., a 20% paste (5) of copper phthalocyanine then added, and the mixture finally ball-milled for 3 hr. Cotton fabric impregnated with this dispersion when heated for 5 min. at 150°c., had excellent fastness to wet and dry rubbing and very good fastness to repeated laundering. There was very slight increase in stiffness. C. O. C.

Pigment-coloured Yarns and Fabrics. Courtaulds Ltd., J. Boulton, C. C. Wilcock, H. Gorge, and H. W. Best-Gordon. *B.P.* 625,609.

Pigment-coloured yarns and fabrics having improved resistance to washing and rubbing are obtained by applying to the yarn or fabric an aqueous dispersion of a finely divided pigment and containing 2–4% on its weight of alginic acid or a water-soluble metal alginate, drying, and then treating so as to insolubilise the alginic compound. This may be done by treating the impregnated fabric with formaldehyde, hexamethylenetetramine, or paraformaldehyde or with a suitable metal salt, e.g. chromic chloride, lead acetate, or aluminium hexaformate. Combination of both treatments gives better results than either alone. If desired, the organic insolubilising agent can be incorporated into the pigment dispersion. C. O. C.

Pigment Colouring. Courtaulds Ltd., J. Boulton, H. Gorge, and C. Ford. *B.P.* 625,215.

Pigment-coloured fabrics of improved resistance to washing and rubbing are obtained by applying to them an aqueous dispersion containing a finely divided pigment, polyvinyl chloride or polyvinylbutyral, and a precondensed, fusible melamine- or urea–formaldehyde resin and then heat-curing. The proportion of the polyvinyl to the formaldehyde resin is approx. 3 : 1. C. O. C.

Colouring Cellulose Acetate. United Turkey Red Co. Ltd., and G. D. Sutton. *B.P.* 592,858.

This specification has been amended (cf. J.S.D.C., **64**, 128 (March 1948)). The use is disclaimed of lakes or inorganic pigments and of thiocyanates other than those of sodium, potassium, calcium and barium. The liquor must be free from compounds of heavy metals. C. O. C.

Fluorescent Red Acetate Rayon. R. G. Dort and Celanese Corpn. of America. *U.S.P.* 2,457,808.

Fluorescent red acetate rayon of high colour intensity in both visible and ultra-violet radiation contains finely divided red-fluorescing zinc sulphide and is dyed in an aqueous bath containing the hydrochloride of diethyl-*m*-aminophenolphthalein and formic acid. C. O. C.

Fluorescent Acetate Rayon. R. R. Sitzler, G. E. Dennison, and Celanese Corpn. of America. *U.S.P.* 2,457,838.

Acetate rayon turning the same colour in both visible and ultra-violet radiation contains a finely divided fluorescent pigment and is dyed with a dye of excellent resistance to change in hue on prolonged exposure to ultra-violet radiation, the pigment and the dye used being such that together they yield the same hue when viewed in either visible or ultra-violet radiation. Thus a red is obtained by using a red-fluorescing zinc sulphide pigment and *p*-nitrobenzeneazo-4-methyl-2-bishydroxyethylaminobenzene, and a yellow with a yellow-fluorescing zinc sulphide–cadmium sulphide pigment and the azo dye obtained by coupling *p*-aminoacetanilide with *p*-cresol or with Artol Yellow SG. C. O. C.

Dyeing Nylon. Courtaulds Ltd., J. Boulton, and E. E. Bowker. *B.P.* 626,517.

The dyeings obtained by treating nylon in an aqueous dispersion of an unreduced vat dye in presence of a swelling

agent but in absence of a reducing agent have better fastness to light than those obtained by the usual reduction process. Thus nylon dyed for 30 min. at 95°c. in a bath containing, on the weight of the nylon, 5% Caledon Yellow GN 300% pdr. and 1% of a fatty alcohol–ethylene oxide condensate dispersed in an 8% aqueous sulphuric acid solution using a liquor ratio of 40 : 1 showed no alteration in hue after 30 hr. in the Fadeometer, whereas a similar pattern dyed by the usual reduction method showed very pronounced change after 30 min. C. O. C.

Dyeing Glass Fibres. Ciba Ltd. *B.P.* 624,453.

Glass fibres treated with a water-soluble condensate of formaldehyde and an acrylic compound of the urea group which contains at least one $-N{:}C(N<)_2$ group and no element of at. wt. > 16 and in which the atomic ratio of oxygen, when present, to carbon is $< 1 : 1$, e.g. dicyandiamidine, are given affinity for acid and direct dyes. By treating with a hardenable aminoplastic precondensate, e.g. dimethylol urea, during or after dyeing, dyeings of good fastness to water and of good colour value are obtained, the fastness to washing being frequently enhanced. C. O. C.

Modern Trends in Piecegoods Preparation, Dyeing, and Finishing. C. N. Rabold. (VII, p. 81.)

Improvement of the Light- and Weather-resisting Properties of Wool Fabrics. A. M. Serebryakov and V. A. Berezina. (X, p. 86.)

IX— PRINTING

Requirements of Petroleum Solvents in Pigmented Textile Printing Pastes. R. A. Billmeier. *Amer. Dyestuff Rep.*, **37**, P748–P750, P759, P760 (15th Nov. 1948).

An investigation of the effect of the composition of petroleum thinners, within the boiling range 300–400°F. required for reasonably fast evaporation, on the performance of pigmented resin emulsion printing pastes (Aridye and Sherdye types) has shown that a spirit containing 16–20% aromatics with the balance composed of equal vol. of paraffins and naphthenes gives maximum colour strength along with the optimum balance of good body and reasonably high stability. The body and stability of the emulsion are influenced by the solvent composition; both high and low aromatic contents cause excessive thinning, and stability is greatest at high aromatic and/or naphthene contents, but increased stability is always associated with loss of body. High paraffin contents produce unstable, thin emulsions. W. K. R.

Some Conditions affecting the Application of Vat Colours. American Association of Textile Chemists and Colorists, Rhode Island Section. *Amer. Dyestuff Rep.*, **38**, P69–P75 (24th Jan. 1949).

To account for the fact that certain vat dyes give poor results when printed, factors affecting the application of six satisfactory, four fair, and six unsatisfactory printing dyes were studied. It was found that under suitable conditions, the solubility and substantivity of all the leuco compounds were adequate, but that there were considerable differences in the ease of reduction, particularly with sodium or potassium carbonate and sodium formaldehydesulphoxylate, the poor printing dyes being generally less readily reduced. Although complete reduction could be effected in glycerol and other media, the presence of an adequate amount of moisture was necessary to obtain satisfactory colour yield. Hygroscopic agents materially affected the results obtained in printing, and a method for evaluating their efficiency is described. It is concluded that the vat dyes most satisfactory for printing are those which show the least variation in results under all conditions, and that if optimum conditions are chosen most vat dyes may be printed satisfactorily. W. K. R.

Progress in Screen Printing. J. A. Bley. *Teintex*, **14**, 91–93 (March 1949).

Developments in screen printing are discussed with special reference to Sieger's mechanical screen-printing machine. A hexagonal wheel rotates between two screen-printing tables and carries the screens, permitting two operators facing each other to print simultaneously, with resultant saving in space. B. K.

Textile Printing Techniques. F. S. Richardson. *Amer. Dyestuff Rep.*, **37**, P864–P865 (27th Dec. 1948).

A number of newer printing techniques are discussed, including methods of reproducing photographs on cloth. Offset printing is practised to a limited extent in U.S.A. All photographic methods for reproducing patterns and designs have drawbacks or limitations, and often slight change in design would permit printing on a regular machine with photoengraved rollers. G. L.

PATENTS

Pigment Printing Pastes. G. T. Douglas, A. Lowe, S. Robinson, W. Todd, and I.C.I. Ltd. *B.P.* 622,967.

Pigments are applied to textiles in presence of a compound of general formula $R(O{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}A\}X)_n$ (R = an organic radical, preferably an aliphatic radical; A = a group of atoms forming an aliphatic or heterocyclic tertiary amine; X = the anion of an acid; $n > 1$). Thus cotton fabric is printed by an engraved roller with a paste containing, all parts being by weight, 20% aqueous paste of the pigment obtained by coupling tetrazotised 3:3′-dichlorobenzidine with 1-hydroxyphenyl-3-methyl-5-pyrazolone (15), tristearin-tris-(carbamatomethylpyridinium) trichloride (7·5), 8% gum tragacanth solution (45), and sodium acetate crystals (7·5) dissolved in water (25). The printed cotton is dried, and aged for 8 min. Even, bright orange prints are obtained which have a soft handle and outstanding fastness to washing. C. O. C.

Diazo Printing Pastes. G. T. Douglas, S. T. McQueen, and I.C.I. Ltd. *B.P.* 618,616.

When printing with paste containing stabilised diazo compounds and coupling components, adding an ester of an aliphatic acid to the paste obviates the need for an acidic pre- or aftertreatment and subsequent drying. Thus in one example a mixture (6 parts by weight) of bisacetoaceto-*o*-toluidide and the triazine obtained from 4-chloro-2-toluidine and sarcosine is dissolved in a mixture of β-diethylaminoethanol (12), diethyl tartrate (0·5), and water (21·5), and 8% gum tragacanth thickening (60) is added. The resulting paste is printed on cotton fabric, dried, aged in steam at 100–102°c. for 15 min., rinsed in water, treated in 0·2% soap solution, rinsed, and dried. A full bright yellow pattern is obtained. C. O. C.

Diazotype Material for Intermediate Prints. General Aniline & Film Corpn. and W. D. Peterson. *B.P.* 625,999.

Control of Contrast in Diazotype Materials. C. Botkin, S. C. Slifkin, and General Aniline & Film Corpn. *U.S.P.* 2,465,424.

Formation of Multicolour Images in a Single Silver Halide Photographic Emulsion. Kodak Ltd. W. T. Hanson, and T. H. Farrell. *B.P.* 623,872.

Positive Colour Photographic Film. J. H. Coote, A. St. J. Austin, and K. M. Hornsby. *B.P.* 626,897.

Bipack Film for Motion Picture Colour Photography. Du Pont. *B.P.* 623,644.

Barrier Layers for Tripack Colour Photography. G. B. Harrison and Ilford Ltd. *B.P.* 626,724.

Colour Photography. R. D. Bensley. *U.S.P.* 2,473,131.

Colour Photographic Printing Process. Société Nouvelle Pathé Cinéma and J. P. Bertrand. *B.P.* 627,254.

Positive Colour Motion Pictures. Republic Pictures Corpn. *B.P.* 626,979.

Converting Black-and-White or Monochrome Photographs into Multicoloured Pictures. R. M. Haff and General Aniline & Film Corpn. *U.S.P.* 2,461,469.

Electrolytic Production of Coloured Records. H. G. Greig and Radio Corpn. of America. *U.S.P.* 2,451,331.

Printing with Sulphuric Esters of Leuco Vat Dyes. W. B. Hardy, E. M. Hardy, and American Cyanamid Co. *U.S.P.* 2,466,656.

Compounds of general formula—

$$X{\cdot}R^1(SO_3H)_m(OH)_n{\cdot}R^2$$

(R^1 = a benzene or naphthalene radical; R^2 = a saturated lower aliphatic hydrocarbon radical; X = hydrogen or an alkyl or alkoxy radical; $m = 1$ or 2; $n = 1$ or 2, the hydroxyl groups being separated by an uneven number of nuclear carbon atoms when $n = 2$) act as accelerators in printing pastes containing sulphuric ester salts of vat dyes and dichromates. In one example a printing paste is composed of colour (3 parts) (composed of the sodium salt of the bis-sulphuric ester of leucotetrabromoindigo (35 parts), 2-naphthol-1-methane-ω-sulphonic acid (10), and sucrose (6·65)), urea (6), a mixture (3) of acetamide (4), diethylene glycol (4), and furfuryl alcohol (2), water (11), 15% aqueous gum paste (70), 25% ammonia (2), 25% aqueous sodium dichromate (5), and 25% aqueous ammonium chloride (3). This paste is printed on cloth, dried, and aged in hot acetic–formic acid vapour. The prints are soaped and dried. Full colour value is obtained in 1–3 min., whereas if the 2-naphthol-1-methane-ω-sulphonic acid is omitted only 5–10% of the expected strength is produced. C. O. C.

Intaglio Printing on Smooth Non-absorbent Materials. O. S. Hassing. *B.P.* 625,168.

Regenerated cellulose film, metal foil, and similar smooth-surfaced non-absorbent materials are intaglio-printed by holding them against the printing roller by two guide rollers resting against and guiding the back of the material without touching the printing roller. This is done so that the part of the material running to the printing roller forms a small angle with that part leaving the cylinder. The two guiding rollers are turnably mounted on arms pivoted in the frame of the machine and held in position by buffer springs inserted between the arms and the frame. C. O. C.

Printing Acetate Rayon. United Turkey Red Co. Ltd. and ^. D. Sutton. *B.P.* 595,344.

This specification has been amended (cf. J.S.D.C., **64**, 205 (May 1948)). The use is disclaimed of lakes or inorganic pigments and of thiocyanates other than those of sodium, potassium, calcium, and barium. The amount of thiocyanate to be used in the paste is 5–15% by weight, and no compounds of heavy metals are to be present.

Printing Acetate Rayon with Acid and Direct Dyes. C. F. Miller snd Du Pont. *U.S.P.* 2,468,940.

In printing acetate rayon with acid and direct dyes addition of caprolactam (the inner anhydride of 5-amino-hexoic acid) and thiourea to the printing paste results in (1) improved strength and brilliance, (2) improved penetration to the reverse side of the cloth, (3) improved range of dyes that can be used, (4) complete stability of the printing paste, (5) neutral, non-corrosive printing paste, (6) non-hygroscopic character of the paste, so that the printed cloth can be stored indefinitely before ageing without "flushing" out of the printed area, (7) no volatile constituents, (8) particular richness and bloom obtained with blacks, and (9) use of only one printing step. Thus acetate rayon cloth is printed with a paste made up of *Colour Index* No. 289 (4 parts by weight), thiourea (2), caprolactam (3), water (41), and thickener (50). It is then dried, aged for 15 min. in the rapid ager, rinsed in cold water, soaped for 5 min. at 120°F., rinsed, and dried. A deep, rich navy blue print of extreme brightness and penetration is obtained. The resultant print is much stronger and more deeply penetrated than when either assistant is used singly. C. O. C.

Printing of Nylon. General Aniline & Film Corpn., H. H. Bestehorn, and H. W. Grimmel. *B.P.* 624,457.

Alkali-solubilised unsulphonated metallised monoazo dyes having at least one nuclear carboxyl group in non-*ortho* position to the azo bridge, which group when present in an aromatic nucleus attached to the remainder of the dye molecule by a non-oxo-carboxylic linkage being in other than *ortho* position to that linkage, give good prints on nylon when developed in acid steam; e.g. the cobalt complex of the dye obtained by coupling diazotised o-aminophenol with 3-hydroxy-2-naphthoic acid in alkaline medium made into an alkaline paste with a suitable thickener, printed on nylon, dried, aged in acid steam (acetic acid added), soaped, and finished as usual gives red–blue prints of excellent fastness to light, washing, rubbing, and chlorine. Instead of using acid steam, an agent which liberates acid on steaming, e.g. ammonium thiocyanate, may be incorporated in the printing paste. C. O. C.

Patterned Effects on Nylon Materials. R. W. Hardacre and I.C.I. Ltd. *B.P.* 626,419.

Nylon dyed with acid or sulphuric ester dyes can have part or the whole of the dyes removed by printing on to it one or more coloured or colourless organic compounds containing one or more carboxylic, sulphonic, or sulphuric ester groups in amount more than sufficient to saturate the dyed nylon in the areas on which the compound is printed. Thus nylon cloth dyed with 1% Solway Blue BNS is printed with a paste made up of 10% of the sulphuric ester of *N*-ethyl-*N*-β-hydroxyethylaniline, 18% of water, 60% of gum senegal thickening (1:1), 10% of China clay, and 2% of an aqueous emulsion containing 25% of sulphonated sperm oil and 25% of pine oil. It is then dried, steamed for 1–2 hr., rinsed in water, soaped at 60°c. for 5 min., and finally rinsed in water. A pure white effect on a deep blue ground is produced. C. O. C.

Applying Striped Coatings to Fabrics. L. N. Dexter. *B.P.* 626,728.

Apparatus for applying striped coatings to fabrics has a trough extending across the width of the fabric and having a series of open-bottomed cells formed by partitions extending between the front and rear walls of the trough. The fabric passes between the cells, which are fed individually with the appropriate colour. The fabric is kept pressed up against the bottom edges of the cells. The lower edges of the partitions taper to a sharp edge towards the exit ends of the cells. C. O. C.

Transfers for Ceramics. Johnson Matthey & Co. Ltd., F. E. Kerridge, and G. E. Roberts. *B.P.* 624,751.

Pigment-colouring Textiles. Du Pont, M. O. Shows, and P. L. Meunier. (VIII, p. 83.)

Rendering Anionic Coating Materials Adherent to Anionic Bases. H. H. Latham, J. R. Morton, and Morton Chemical Co. (X, p. 89.)

Assessment of Thickening Agents. W. Jülicher. (XIV, p. 97.)

X—SIZING AND FINISHING

Resin Impregnation of Cotton Fabrics for Prevention of Microbiological Decay. ORR 63/49* (PB 86,252).

A report from the Tropical Determination Research Laboratory of the U.S. Quartermaster Depot. Micro-organisms attack cotton from the outer surface inwards in an apparently highly localised manner, and it is assumed that any physical barrier preventing the fungi or bacteria from contacting the cellulose molecules will protect cotton fabric against microbiological attack. A microbiologically resistant coating has been found to be given by resin impregnations, and studies in this field are described. C. O. C.

* Photocopies available from T.I.D.U., Board of Trade, 40 Cadogan Square, London S.W.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.— see J.S.D.C., **66**, p. 53 (Jan. 1950).

Preparation of Winceyettes for Raising without an Emulsion Treatment. V. N. Nebarov. *Tekstil. Prom.*, **8**, 25–26 (Sept. 1948).

In the production of printed winceyettes, treatment in an oil or wax emulsion prior to raising is obviated by modifying the preparation of the fabric so as to retain the natural fats and waxes of the cotton, while at the same time, attaining a satisfactory bleach free from motes. The modification results in a reduction in the cost of processing and in the proportion of faulty goods, while the quality of the raising is excellent. In the works process described the normal procedure included an 8-hr. caustic soda boil under a pressure of 1 atm. and a hypochlorite bleach. The emulsion treatment consisted of a pad through an emulsion of paraffin wax with ammonium soap (total fatty content 3·5%). The fabric was dried and raised to a temperature above the melting-point of the wax immediately before passing into the raising machine. In the revised process the only essential change, apart from the omission of the emulsion treatment, is the replacement

of the caustic soda kier boil by the following treatment—The fabric is impregnated in a solution of caustic soda (3 g./litre) and sodium hypochlorite (0·5–0·7 g. of active chlorine per litre); it is allowed to lie for 2 hr. and then boiled in water for 6 hr. under a pressure not > 1 atm.
A. E. S.

Weathering Characteristics and Rot Resistance of Cotton Duck treated with the Copper Complex of Nitrosophenylhydroxylamine. C. H. Bayley and M. W. Weatherburn. *Canadian J. Res.*, **27F**, 112–118 (March 1949).

Unbleached cotton tentage duck treated with the copper and copper–iron complexes of nitrosophenylhydroxylamine show increased resistance to soil burial tests, but outdoor weathering for three months gave increased actinic degradation and considerable loss of treating compound. Higher concentrations gave increased effects.
W. J. M.

Metallic Oxides as Barrier Treatments for Prevention of Attack by Light on Cellulose. S. L. Perti, S. K. Ranganathan, T. S. Subramanian, and L. R. Sud. *Nature*, **163**, 877–878 (4th June 1949).

Attention is directed to the remarkable effect of manganese (as oxide) in inhibiting photodegradation. Of other metals (as oxides), iron and aluminium show some protective effect in the very early stages of exposure but are not useful, chromium generally follows the pattern of the control in the rate of degradation, while copper, tin, and titanium accelerate degradation. While the result with copper is not surprising, the behaviour of manganese in inhibiting photodegradation has considerable practical possibilities.
H. H. H.

Treatment of Textile Materials with Methyl Silicon Amine to give Improved Resistance to Penetration of Moisture. *J. Council. Sci. Ind. Research* (Australia), **21**, 222 (1948): *Chem. Abs.*, **43**, 4858, 4859 (1949).

Cotton and wool cloths treated with a benzene solution of methylsilylamine showed greatly improved resistance to capillary water absorption. Treatment with ethylsilylamine was less effective.
C. O. C.

Animalisation of Cellulosic Fibres. D. Fornelli. *Amer. Dyestuff Rep.*, **37**, 853–858, 882 (27th Dec. 1948).

A comprehensive review of the methods of animalisation, including incorporation of proteins, non-protein nitrogen-containing substances, and mixtures or reaction products of these two classes. In the second class the use of amines, polyamines, amides, polyamides, and quaternary ammonium salts is discussed, as well as the more recent use of ethyleneimine and its reaction products with di*iso*cyanates. The fastness properties remain the most objectionable feature in dyeing. There are 99 references to the literature.
G. L.

Some Aspects of the Chemical Control of Wool Shrinkage. J. M. Gould. *Amer. Dyestuff Rep.*, **38**, P407–P410 (16th May 1949).

Chemical methods of attaining shrink-resistance in wool are reviewed, and information is given about the washing, bleaching, and dyeing properties of wool which has been chlorinated or treated by the Harriset process.
A. S. F.

Reaction between Wool and Active Chlorine. D. Frishman, L. Hornstein, A. L. Smith, and M. Harris. *Ind. Eng. Chem.*, **40**, 2280–2284 (Dec. 1948).

Reaction between wool and solutions of active chlorine has been studied at three different pH ranges. At pH 1 a large weight loss, destruction of scale structure, and a change in mechanical properties occur. Cystine is destroyed with subsequent loss of sulphur. At pH 3–7 reaction produces either a slight loss or slight gain in weight, but extensive modification occurs. Cystine content is lowest and alkali solubility is highest in this pH range. Treatment at pH 9–11 results in a slight loss in weight and only minor modification of wool protein. Using aqueous hypochlorite at pH 8–9 in the plant, wool was made shrink-resistant with a minimum of fibre modification.
G. L.

Affinities of Water-soluble Substances for Wool and their Antibacterial Activities. R. Fischer, S. Seidenberg, and V. P. Weis. *Helv. Chim. Acta*, **32**, 8–17 (Feb. 1949).

In the literature certain similarities are recorded between wool and bacteria, and on this ground the affinities for wool of the following wetting, washing, mothproofing, and disinfecting agents—bile acid, Tinopol Oil BH, Tinovelin B, Eriopon AC, Aerosol OT, Desogen, Emulphor O, Mitin FF, and Eulan N—have been investigated. Correlation has been established between affinity and antibacterial activity, and prospective future developments are envisaged.
H. H. H.

Reactivity of the Sulphur Linkage in Wool. A. J. Farnworth and J. B. Speakman. *Nature*, **163**, 798–799 (21st May 1949).

It had been shown that the disulphide bond breakdown in wool fibres is responsible for their resistance to felting after treatment by chlorine. The sodium hydroxide treatment used in showing this has since been called into doubt, and it has been thought necessary to confirm the theory by potassium cyanide treatment. This converts the cystine to lanthionine with an increase in stability to chlorine. It was found that subsequent chlorination did not increase the resistance to felting, thus confirming the above theory.
W. J. M.

Cross-linking Reduced Animal Fibres. W. J. P. Neish and J. B. Speakman. *Nature*, **164**, 708 (22nd Oct. 1949).

Load–extension tests with reduced human hair fibres show that allyl *iso*thiocyanate is even more effective in cross-linking such fibres than oxidising agents, metal salts, or certain organic halogen compounds.
W. J. M.

Protection of Wool against Insects by Mitin FF and DDT. R. Burgess. *J.S.C.I.*, **68**, 121–126 (April 1949).

A brief review is given of moth and carpet beetle damage and methods of prevention. A study of the protection given by Mitin FF (Gy) has been made, and it is concluded that it acts as a stomach poison, kills moth larvæ of all ages and newly hatched carpet beetle larvæ, and repels older carpet beetle larvæ. DDT kills adult clothes moths by contact slowly, and newly hatched larvæ rapidly. Older larvæ are killed probably by combined contact and stomach poisoning. It repels and adversely affects half-grown larvæ of carpet beetles.
W. J. M.

Improvement of the Light- and Weather-resisting Properties of Wool Fabrics. A. M. Serebryakov and V. A. Berezina. *Tekstil. Prom.*, **8**, 49–51 (July 1948).

Wool fabric, treated in various ways, was exposed to light and weather, and examined for changes in tensile properties. Dyeing with acid dyes of the triphenylmethane or azine class generally results in increased tendering on exposure. Such dyes are the following—Acid Green (*Colour Index*, No. 660), Acid Violet (*C.I.* 697), Patent Blue A (*C.I.* 714), Brilliant Milling Green B (*C.I.* 667), Safranine (*C.I.* 841), and Wool Fast Blue (*C.I.* 833). The azoxy–azo dye Direct Yellow R (*C.I.* 620) is also a tenderer, but azo dyes in general exert a protective effect. Examples of dyes giving considerable protection are—Acid Chrome Black (*C.I.* 299), Acid Chrome Yellow (*C.I.* 195), and Acid Brilliant Red (*C.I.* 31). It is recommended that the use of dyes found to be deleterious should be discontinued in all cases where a satisfactory substitute can be found. A reduction of the tendering of undyed wool on exposure is obtained by treatment with a solution of tannin, copper sulphate and sodium dichromate, or by treatment with a urea–formaldehyde, phenol–formaldehyde or acrylic condensate. Chromium fluoride solution is very effective, and it is recommended that it be used whenever possible in place of sodium dichromate in the chroming process.
A. E. S.

Factors Influencing the Raising of Wool Fabrics. C. S. Whewell and J. B. Crawford. *J. Textile Inst.*, **40**, T 341 (May 1949).

Teepol (Shell) (an aqueous solution of sulphated olefins), is found to promote the raising of wool fabrics. If this is due to a lubricating action, anti-lubricants would be expected to reduce susceptibility to raising. It has been found that the anti-lubricant Syton (Monsanto) (a dispersion of silica) does, in fact, retard raising.
W. J. M.

Finishing Crossbred Heavy Twills. Anon. *Wool Record*, **75**, 1415, 1417, 1419 (19th May 1949).

One of the biggest difficulties in preparing crossbred heavy twills for dyeing is that of obtaining adequate softening. Production here is second in importance to finish and handle, and the goods must be given long enough

in each process. In a milled finish the handle is easier to obtain owing to the amount of cover on the cloth, which give a softness which cannot be achieved by a clear cut finish. If cutting is insufficient, the twill looks flattened and the finish mashy, and there is a tendency to rub up. Insufficient cutting helps to hide poor or inadequate wet processing and the cloths are often "glazy", the finish being entirely upon the surface of the fabric. Finish cannot be placed upon a fabric by dry finishing, which should bring out to the full the benefits imparted to the cloth by the wet processes. With crossbred twills of 18–22 oz. finished weight, it is essential from both a softening and a dyeing point of view to obtain the utmost penetration of the cloth. They should therefore be both crabbed and steamed. Crabbing, apart from other considerations, helps greatly in the penetration of the cloth, but care has to be taken neither to flatten the twill nor to make the goods feel thin. Not more than 2 or 3 pieces should be crabbed on a roll. The top-weight roller must not be used, and the drag-weight must not be > 60 lb. There should be an 8–10-yd. wrapper sewn to each end of a batch. The goods should be thoroughly boiled in each bowl and kept revolving all the time. For steaming the pressure should not exceed 9 lb./sq. in., and the roll should be kept revolving and the wrappers securely fastened down. Steaming lasts 15 min. from the first emergence of steam from the outside wrapper. The goods are then rerolled and steamed again. They are then allowed to cool naturally, care being taken that there is adequate air space all round the roll. The strength of alkali used for scouring is 5–7°Tw. for crossbreds. By strengthening the alkali solution some softening of the goods is obtained, but only to a limited extent. It is better to use more alkali than increase its strength. A double or split scour is best, and it is advisable before finishing off the scour to give 15–20 min. crushing in the milling machine. A better scour and a more stable scouring bath are obtained if the goods have been crabbed. The pieces are well scoured with soap and alkali for 45–60 min. and then washed off for 15 min. with water at 90–100°F. This wash-off is incomplete, as it is desirable to keep up the alkali content of the goods. They are then hydroextracted and crushed in 2 or 3 drafts as the milling machine allows. There should be no weight on the lid of the trough, but the lid should be low enough to ensure free and unobstructed passage through the trough. No added soap or alkali is required for this crushing. The pieces are then replaced in the dolly and worked with soap and ammonia, a quart of ammonia in 2 gal. aired water for each piece. They are scoured for 35–45 min., washed off with water at 110–120°F., for 90–120 min., and well cooled before being hydroextracted. The goods should be steamed and brushed, and as well set up for cutting as possible. The backs are cut first, being given 3 or 4 cuts on a rubber-, spring-, or cushion-bed machine to produce a "baulk" back, i.e. to leave a slight cover on the back. This imparts a firm thick handle. The face is then given 2 or 3 cuts on the same machine and then finished off with 1 or 2 cuts, according to pattern, on a solid-bed machine. The twill should now be bold and clear and not mushy or inclined to rub up. The pieces are then blown from each end, run off warm without cooling, and lightly steamed to remove creases. Damping follows, and even with the finest of sprays a considerable proportion of water remains on the surface for some time, so that if a spray damper is used, then the goods should be allowed to lie in folds for at least 12 hr. It is better to use medium-type wrapper damping, for then there is no risk of surface glazing as there is with spray damping. The pieces are then rigged up face inside and pressed with a paper on the face as well as on the back. Each piece should be broken in the press by three warm wrought-iron press plates, and 25 cwt. applied in the flat pressing. The aim is not merely to gain finish but to reduce loss of moisture to a minimum and so retard sweating and cooling down of the piece in order to obtain working of finish within the fabric and not surface glaze. The goods require turning to avoid raw cuttle marks and should finally be cold-flatted. The final finish may be to open out after pressing, steam lightly on the face for condition, and then cramp overnight under medium weight. C. O. C.

History of our Home Finishing Industry. I. G. Ioffe. *Tekstil. Prom.*, 8, 23–25 (Sept. 1948).

The idea that the Russian dyeing, printing, and finishing industry was developed in accordance with Western European models without any considerable participation of initiative or inventive skill on the part of native workers is stated to have been prevalent before the Revolution and to be widespread even now. In support of the contrary view the writer gives a survey of Russian achievements from the twelfth century onwards. One of the topics is the outstanding rôle of Russian chemists in the development of synthetic dyes. A cardinal step was the commercial production of aniline, made possible by the work of N. N. Zinin, who discovered the preparation of aniline from nitrobenzene in 1842. In 1856, the year of the discovery of Mauve, the Russian chemist Y. Natanson made Fuchsine by heating aniline with ethylene dichloride; the claim that Perkin prepared the first synthetic dye must be placed in doubt. In the seventies M. L. Losev produced the first non-tendering steam Aniline Black, and in the same period, prior to work in this field by Prud'homme, N. G. Volchaninov developed the reserve style of printing on an Aniline Black ground. At about the same time N. N. Voznesensky discovered the one-bath method of dyeing basic colours, in which resorcinol is employed to delay the combination of the dye with tannic acid. Another important advance in dyeing technique is attributed to M. A. Ilyinsky, who in 1911 invented the two-phase method of dyeing, which includes, as a special case, the pigment-pad process for vat dyes, now universal. Important contributions were made to the discharge style of printing. Thus the use of anthraquinone as a catalyst in the discharge printing of α-naphthylamine bordeaux was discovered by S. V. Zlatoustovsky in 1906, and the development of Leucotrope O, which was put on the market by the Badische Anilin- und Soda-Fabrik, was the result of the work of A. E. Poray-Koshits in 1910 on the discharge printing of Indigo and other vat grounds. A number of contributions in other fields, including plant, are discussed. A. E. S.

Resin Finishing of Textile Fabrics. R. G. Thomas. *Amer. Dyestuff Rep.*, 38, P 413–P 416 (16th May 1949).

The properties and uses of thermoplastic and thermosetting resins are compared, with emphasis on their use in producing effects on textiles such as modification of handle, dimensional stability, increased wet-strength, and improvements in the fastness of direct cotton dyeings. The main improvement anticipated in future research on resins of these types is resistance to chlorination. A. S. F.

PATENTS

Improving the Tensile Strength of Cotton Fibres, Yarns, and Cords. United States Rubber Co. *B.P.* 625,184.

The tensile strength of natural cellulosic fibres is improved by treating them with an aqueous solution containing an alkali-metal salt of a *cyclo*alkanecarboxylic acid, e.g. sodium naphthenate, stretching them to just below their breaking point while still wet, and drying before releasing the tension. C. O. C.

Resin-bonded Cellulosic Yarns or Cords. Wingfoot Corpn. *B.P.* 625,937.

The tensile strength and fatigue resistance of cellulosic yarns or cords is improved by bonding the fibres together with a mixture of phenol–formaldehyde resole (100 parts by weight) and an alkali-metal rosinate (25–400) and curing at 300–600°F. C. O. C.

Setting Highly Twisted Yarns. Industrial Rayon Corpn. *B.P.* 625,096.

Highly twisted yarns, e.g. tyre cord material, are given a set to ensure greater controllability during subsequent processing, by passing in the form of comparatively large cones between high-frequency electrodes, which heat them evenly to a suitable temperature, e.g. 70°C. In one example a cone containing approx. 18·5 lb. of tyre cord is so heated for 15 min. J. W. B.

Treating Yarns or Fabrics with Colloidal Silica to reduce Slippage, increase Tensile Strength, and improve the Finish. Monsanto Chemical Co. *B.P.* 626,847.

The materials are treated with a silica sol containing neither an electrolyte nor silica gel so as to take up 0·1–10·0% of their weight of silica. C. O. C.

Improving the Tensile Strength of Grey Cotton Yarn. L. Axford and United States Rubber Co. *U.S.P.* 2,471,554.

The tensile strength of grey cotton yarn is improved by saturating the yarn at 60–100°c. with a mixture of 10–50% of water and 90–50% of a saturated C_{3-5} monohydric alcohol which can dissolve 10% of its weight of water at 75–95°c. The yarn is subjected while saturated with the hot liquor to a tension of 50–75% of the breaking strength of the raw yarn measured at 65% R.H. and 70°F. The yarn, still under tension, is finally dried at a temperature high enough to volatilise both the water and the alcohol. C. O. C.

Scouring Cellulosic Textiles with the use of Steam. G. P. Vincent, A. L. Dubeau, and Mathieson Chemical Corpn. *U.S.P.* 2,469,249.

In the scouring of cellulosic textiles by impregnating them with an aqueous scouring liquor, steaming, and then transporting to a washing machine, better results are obtained if they are kept at not < 140°F. during their passage from the steaming chamber to the washing machine. C. O. C.

Reducing the Felting Power of Wool. J. B. Rust and Montclair Research Corpn. *U.S.P.* 2,467,233.

The felting power of wool is reduced without impairing its handle by treating it with an aqueous emulsion containing a 100% polymerised 1:3-butadiene polymer and a urea- and/or melamine–formaldehyde resin. The ratio of resin to polymer is 4 : 1 to 1 : 1·2 for a urea–formaldehyde resin and 3·1 : 1 to 1 : 1·2 for a melamine–formaldehyde resin. The wool has to take up 1–50% of its weight of solids, the amount of the polymer to be absorbed being 2–15% on the weight of the wool. The emulsion also contains a non-cationic emulsifying agent and not < 25% on the weight of the polymer of a water-soluble neutral salt of an alkali metal, and its pH must be < 7. C. O. C.

Reducing the Felting Power of Wool. D. Frishman, M. Harris, and Harris Research Laboratories. *U.S.P.* 2,466,695.

The felting power of wool is reduced by treatment with a hypochlorite solution of pH 7·5–9·0 containing 1–6% available chlorine, for 1–60 sec., followed by immediate dechloring. Thus flannel is padded through a sodium hypochlorite solution at 20°c. containing 3% of available chlorine, 0·8% of Tergitol 4, and enough sulphuric acid to bring it to pH 8·5. The squeeze is adjusted so that the flannel takes up 60% of its weight of the solution and the time between entering the liquor and entering the nip is 2·3 sec. The flannel passes immediately from the nip into a 1% solution of sodium bisulphite and is then rinsed with running water. A 10·5-oz. flannel so treated shrank only 1%, whereas an untreated sample shrank 39%, in area in an accelerated laundering test. C. O. C.

Reducing the Felting Power of Wool by Use of Chloroprene Polymers. J. B. Rust and Montclair Research Corpn. *U.S.P.* 2,471,456.

Wool is rendered non-felting without impairment of its handle by treating it in an aqueous emulsion at pH < 7 containing a copolymer of 0–40% by weight of an alkyl acrylate or butadiene and 100–60% of chloroprene, a non-cationic emulsifying agent, and not < 25% by weight on the polymer of a water-soluble neutral salt of an alkali metal. The wool has to absorb 1–25% by weight of the polymer. C. O. C.

Treating Textiles with Alkali-metal Zincate Solutions of Cellulose Ethers— Regenerated Cellulose Ether Rayon. S. M. Edelstein. *U.S.P.* 2,465,520.

Various finishes may be obtained on textiles of all kinds by treating them first with a cellulose ether dissolved in an aqueous solution of an alkali-metal zincate and then with a mercerising lye so as to precipitate the cellulose ether on the fibres. Regenerated cellulose ether rayon may be obtained by extruding a solution of a cellulose ether in aqueous alkali-metal zincate into a coagulating bath, e.g. a bath containing sulphuric acid and sodium sulphate. C. O. C.

Dimensional Stabilisation and Crease-resisting of Fabrics Wholly or Mainly Composed of Regenerated Cellulose. Cluett, Peabody & Co. Inc. *B.P.* 624,733.

Fabric composed wholly or mainly of regenerated cellulose is given dimensional stability and crease-resistance by treating it with an aqueous solution of pH 1·0–2·5 and containing the equivalent of 30–200 c.c. of 30% by weight glyoxal solution and 1–20 g. of an acidic catalyst per litre, the glyoxal content exceeding the equivalent of 120 c.c. of 30% glyoxal solution and/or that of the acidic catalyst exceeding 4 g. per litre, and then baking at not < 212°F. for a time interval inversely related to the temperature, so as to cause the glyoxal to react with the regenerated cellulose. Thus a 100% spun viscose rayon cloth, 4 oz./yd., was impregnated with 130% of its weight of an aqueous solution at pH 1·25 containing per litre 120 c.c. of 30% glyoxal solution and 15 g. of oxalic acid, dried at 250°F. to the specified dimensions, and cured at 300°F. for 5 min. After washing and slack drying it had a residual shrinkage of < 1%. C. O. C.

Reducing the Swelling Value of Viscose and Casein Rayons. J. G. Weeldenburg and American Enka Corpn. *U.S.P.* 2,468,530.

The swelling value of viscose rayon is reduced and the water-repellency and wet strength are increased by treating it with an aqueous solution of a preformed monomeric mono- or di-methylol derivative of a mono- or di-substituted phenol, respectively, formed by formaldehyde treatment of a substituted phenol in which 1 or 2 of the 3 reactive hydrogen atoms in the *para* and *ortho* positions has been substituted by methyl or chlorine, and finally heat-curing the impregnated rayon. Thus viscose rayon fabric was treated with 2:6-dimethylol-4-methylphenol and cured at 130°c. for 2 hr. A sample of the treated material 1 cm. sq. remained floating on water for several days, whereas an untreated sample sank within a few minutes.

U.S.P. 2,468,531.

The process is applied to casein rayon. C. O. C.

Nitrating Cellulose Lace-backing Fabrics. J. Datlow. *U.S.P.* 2,461,632.

Lace-backing fabric of improved tensile strength, resistant to deterioration on storing in presence of agents promoting conditions of mildew, of low inflammability, and readily disintegrated in alkali is obtained by treating a natural cellulose, open-mesh fabric with a liquor containing in parts by volume 97% nitric acid (60–40) and 75% phosphoric acid (40–60) for 30 sec., exposing the treated fabric to air for 4·5 min., and finally washing with dilute aqueous alkali. C. O. C.

Treating Fibrous Cellulosic Materials with 3:4-Epoxy-1-butene. D. M. Musser and Pacific Mills. *U.S.P.* 2,455,083.

On treating cellulosic materials containing free hydroxyl groups with 3:4-epoxyl-1-butene in presence of alkali the highly reactive 2-hydroxy-Δ3-butenyl ether of cellulose is obtained. This may then be treated so as to saturate the double bond. Thus oxidation with dilute aqueous potassium permanganate yields the 2:3:4-trihydroxybutyl ether of cellulose, which has great affinity for water. If a water-repellent finish with a soft handle is desired then the double bond is saturated with alkyl groups. The treatment of cellulosic textiles with epoxy-alkenes thus forms a very convenient basic treatment preparatory to treatment with other compounds, which may or may not react with native cellulose, to impart any one of a very wide range of durable finishes. C. O. C.

Randomly Quilted Effect on Fabrics containing Thermoplastic Yarns. British Celanese Ltd. *B.P.* 624,720.

Randomly quilted and similar buckled effects are obtained on fabrics consisting wholly or mainly of thermoplastic yarns by passing them while untensioned and unconstrained across a hot unpatterned plate. If the thermoplastic yarn is acetate rayon the temperature of the plate is preferably 250–280°c., and the time of contact 1–5 sec. C. O. C.

Crinkled Ribbon- or Mat-like Fabrics. R. J. Taylor and American Viscose Corpn. *U.S.P.* 2,461,094.

Crinkled ribbon- or mat-like fabrics are produced by longitudinally stretching a wet web of continuous filaments, some of which are in a plastic condition while others are in an elastic condition, forming the web while still wet into a multilayered winding, severing the winding across its width, drying the relaxed winding in the form of a band, and finally stretching the dried band in width while permitting it to expand in thickness. C. O. C.

Napped Woven Fabrics having a Leathery Handle. F. H. Russell and Pepperell Manufacturing Co. *U.S.P.* 2,469,245.

Fabric having a leathery handle and finish is obtained by raising it so that the nap fibres are projected outwards and parallel to one another, and then bending the free ends of the nap fibres inwardly toward the fabric so that they interlock with adjacent nap fibres. The nap is then treated with a resinous liquid, the resin cured, and the treated fabric subjected to gradual flexing. Suitable apparatus is described with the aid of diagrams. C. O. C.

Rendering Anionic Coating Materials Adherent to Anionic Bases. H. H. Latham, J. R. Morton, and Morton Chemical Co. *U.S.P.* 2,468,086.

Better adhesion of anionic coatings to anionic bases is obtained if the latter are first treated with an aqueous solution of a cation-active compound made by reaction of 1–3 mol. of an alkyl sulphate, phosphate, or halide, having 1–3 carbon atoms in the alkyl group with a dehydration–amidation product made by heat-condensing 1–5 mol. of a straight-chain alkylenepolyamine of general formula—$NH_2{\cdot}[C_2H_4{\cdot}NH]_x{\cdot}C_2H_4{\cdot}NH_2$ or $NH_2{\cdot}[C_2H_4{\cdot}NH]_y{\cdot}C_2H_4{\cdot}NH_2$ (x = 1–41, y = 1 or 2) or an alkylenepolyamine derived from 1:3-butanediamine with 1–3 mol. of tall-oil acid, a C_{6-10} fatty acid, a monohydroxy-substituted C_{6-10} fatty acid, or a C_{4-10} dicarboxylic acid so as to distil off 1–10 mol. of water. On coating the treated base with an aqueous emulsion of an anion-active film-forming material, the cationic compound neutralises the anionic activity of the film-forming material, so that the latter is firmly bonded to the base by the ionic activity of the cationic compound with both the base and the coating. The method is particularly applicable to the coating of all types of fibres, especially to the coating of tyre cords and fabrics with latex emulsions. Used in pigment printing or organic colour printing from emulsions of oil-in-water type, increased fastness to abrasion, rubbing, and washing is obtained. C. O. C.

Flexible Sized or Impregnated Sheet Material suitable as a Base for Artificial Leather, Adhesive Sheets, or Tape. Minnesota Mining & Manufacturing Co. *B.P.* 624,929.

Base material for artificial leather, etc. is obtained by impregnating a porous fibrous fabric with broken-down rubber, 25–400% on the weight of the rubber of a resin, a self-vulcanising organic accelerator and an activator for it, and then vulcanising. C. O. C.

Transparent or Translucent Coated Fabric for Use as Glazing Material. British Celanese Ltd. *B.P.* 626,513.

An open-mesh woven or net fabric made of fibres of a vinyl or vinylidene polymer is coated with a cellulose ester of a carboxylic acid or a cellulose ether so as to fill the interstices of the fabric. C. O. C.

Laminated Materials. R. H. Barnard. *B.P.* 624,716.

Molten fibre-forming material is extruded through a number of serially arranged groups of small orifices, and the extruded material from one group continuously placed as a layer on a layer of material extruded from the preceding group. Each layer is subject to pressure before another layer is placed on it and/or the whole is pressed following the placement of the last layer. The material extruded may be the same for all groups, or one or more groups may extrude material different from that being extruded from the others. Another material, e.g. felt or regenerated cellulose sheeting, may be placed between two or more of the layers. C. O. C.

Dimensional Stabilisation of Textiles. J. E. Lynn, L. A. Fluck, and American Cyanamid Co. *U.S.P.* 2,466,457.

Textiles, of all fibres, are rendered dimensionally stable by impregnating them with an aqueous dispersion of a curable alkylated methylolmelamine and with 1–10% on their dry weight of urea and/or thiourea and then heat-curing. Thus an all-wool flannel was impregnated with an aqueous solution of methylated methylol melamine containing 0·4% of diammonium hydrogen phosphate on the dry weight of the resin and 3–6% of a mixture of urea and thiourea, and then dried and cured for 9 min. at 290°F. The finished flannel had increased tensile strength and excellent dimensional stability even after repeated washings. C. O. C.

Dimensional Stabilisation of Fabrics. Standfast Dyers & Printers Ltd. and W. Kilby. *B.P.* 626,336.

Wet fabric is stretched weftwise to more than loom width while allowing free contraction warpwise. The tension is then relaxed, and the fabric dried while free from tension in both warp and weft. C. O. C.

Stiff Water-repellent Finish. J. R. F. Jackson, A. H. Ford, and I.C.I. Ltd. *B.P.* 627,356.

Stiff water-repellent finishes are obtained by use of starch and a wax emulsion simultaneously with or before treatment with glyoxal. Thus, all parts being by weight, maize starch (50) is heated with water (950) at 100°c. until the starch is swollen, and is then stirred into a mixture of Dispanil V (200) and water (800). 30% Aqueous glyoxal (10) is then stirred in. Cotton gaberdine is impregnated with the resulting composition at 50–60°c., and partly dried in air at 60–80°c., drying being completed on cans at 110°c. The treated fabric is stiff and highly water-repellent. C. O. C.

Wash-fast Stiff Finish. D. H. Powers, E. H. Rossin, and Monsanto Chemical Co. *U.S.P.* 2,469,407.

A stiff finish which resists repeated washings is obtained by using an aqueous solution of an alkylenepolyamine and an ammonium or amine salt of a styrene–maleic anhydride copolymer and then drying to set the resin. The amount of polyamine used is 5–30% on the weight of the salt of the copolymer. It may be applied at any stage of processing from the loose fibre to the dyed or printed fabric.

U.S.P. 2,469,408.

The solution used contains an ammonium salt of a styrene–maleic anhydride copolymer and 2–20% on the weight of that salt of a water-soluble alkyl ether of methylolmelamine. The fabric must absorb 2–15% by weight of the salt.

U.S.P. 2,469,409.

The solution used contains an ammonium or amine salt of a copolymer of styrene or a substituted styrene with maleic anhydride or an incompletely esterified maleic anhydride and 1–20% on the weight of the salt of formaldehyde or a water-soluble formaldehyde polymer. The fabric must absorb 2–15% by weight of the salt. C. O. C.

Rendering Textiles Shrink-resistant and/or Water-repellent. W. Baird, T. Barr, A. Lowe, J. Oliver, and I.C.I. Ltd. *B.P.* 619,536.

Compounds of general formula $R^1(O{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}OR^2)_3$ (R^1 = a substituted or unsubstituted aliphatic radical, R^2 = hydrogen or alkyl), obtainable from tricarbamates of general formula $R^1(O{\cdot}CO{\cdot}NH_2)_3$, e.g. by heating with formaldehyde, are soluble or readily dispersible in water and soluble in organic compounds. On heating at > 100°c., under acid conditions, they decompose to yield water-insoluble substances. They are used for imparting shrink-resistance and/or water-repellency to textiles, being especially suitable for use on wool materials. In one example, all parts being by weight, tristearin-11:11′:11″-triol tricarbamate (100) (obtained by treating hydrogenated castor oil with phosgene and then with ammonia) in benzene (240) is mixed with paraformaldehyde (10) and anhydrous potassium carbonate (20), and the mixture stirred for 2–3 hr. at 50–60°c. The filtrate is evaporated at 45–50°c. under reduced pressure. In the resulting yellow oil (20) is dissolved the condensate (1) of 1 mol. of cetyl alcohol with 17 mol. of ethylene oxide, and the solution is then emulsified with water (79). 1·5 N. Hydrochloric acid (100) is then added. Light-weight wool flannel impregnated with its own weight of this emulsion, dried at 50°c., and then baked at 145°c., shrinks only 11·2% in area on hand milling in 5% soap solution for 15 min., whereas the untreated flannel shrinks 31·9%. C. O. C.

Rendering Textiles and other Solid Materials Water-repellent. British Thomson-Houston Co. Ltd. *B.P.* 621,970.

Textiles and other solid materials are rendered water-repellent by impregnating them with a siliconate obtained by dissolving the hydrolysis product of an alkyl- or aryltrihalogenosilane in an aqueous solution of an alkali-metal hydroxide. The water-repellent finish obtained is as good as that given by treatment with organosilicon halides and has the advantage of causing little or no loss of strength to cellulosic materials. C. O. C.

Rendering Textiles Water-repellent. H. L. Van Mater and National Lead Co. *U.S.P.* 2,457,853.

Textiles are rendered water-repellent by impregnating them with a solution containing a double carbonate of zirconium and soap, the amounts of each component being such as to allow formation of a zirconyl monofatty acid compound, at a temperature below that at which such a compound is formed, and then heating the impregnated materials to $> 60°$c. so as to precipitate such a compound in the fibres. Thus in one example ammonium carbonate (56·8 g.) is dissolved in water (500 ml.) at room temperature, and zirconium sulphate crystals (40 g.) are stirred in. Sodium oleate (34·4 g.) is dissolved in water (500 ml.) at 80°c., and the solution cooled to 40–50°c., and then mixed with the first solution. Material to be made water-repellent is then worked in the solution for 30–60 sec., and after removal of excess liquor dried at 80–100°c., being finally rinsed in water to remove the by-product salts. The finish is fast to washing and dry cleaning. C. O. C.

Rendering Textiles resistant to Attack by Insects. Hercules Powder Co. and C. A. Buntin. *B.P.* 624,176.

Textiles are rendered immune to clothes moths and black carpet and furniture carpet beetles by impregnating them with a bicyclic polychloroterpene containing 60–70% chlorine dissolved in an inert solvent, e.g. with 0·8% of a polychlorocamphene containing 67·3% chlorine. C. O. C.

Smooth Glazed Yarns or Fabrics containing Non-thermoplastic Fibres and Fibres of Polythene or Hydrolysed Ethylene–Vinyl Acetate Copolymer. A. H. Little and I.C.I. Ltd. *B.P.* 623,805.

A smooth glazed finish is imparted to yarns or fabrics containing as the chief constituent a fibre which changes in neither shape nor strength when heated for a short time below 200°c., e.g. cotton, wool, or nylon, and as the minor constituent fibres of polythene or of a hydrolysed copolymer of ethylene and vinyl acetate, by heating them to a temperature at which the minor constituent has a melt viscosity $< 50{,}000$ poises, and then cooling, either during or after the application of pressure. C. O. C.

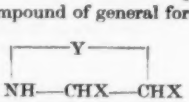
Coating Fabric with a Modified Halogenoprene Composition. R. N. MacDonald, H. S. Rothrock, and Du Pont. *U.S.P.* 2,465,336.

Tough, dense, highly abrasion-resistant coatings are obtained on fabrics by use of compositions containing 95 parts of polymerised 2-bromo- or 2-chloro-1:3-butadiene and 5 parts of brominated or chlorinated polyethylene and then curing. Thus, all parts being by weight, 2-chlorine-1:3-butadiene plastic polymer (400), zinc oxide (180), magnesium oxide (150), calcium carbonate (150), and pigments (60) are milled together, and then 68% chlorinated polyethylene (42·5) is added to the mixture (200) together with a solvent. The product is coated on to cotton fabric so as to deposit 13 oz. of non-volatile matter per yd. 50 in. wide, and then vulcanised by heating for 2 hr. C. O. C.

Impregnating Fibres with Silver. G. Schwartz. *U.S.P.* 2,459,896.

Organic fibres are given outstanding fungicidal and bactericidal properties by impregnating them with yellow, highly dispersed colloidal silver by treatment with an aqueous solution of a silver salt in presence of a hydroxy alkylamine. Thus in one example cotton gauze is impregnated in a solution containing per litre of water 10 g. silver oxide and 10 g. 2-amino-2-methylpropanol and then subjected to radiant heat lamps in a moist atmosphere, being finally washed and dried. The treated material is suitable as highly bactericidal bandages. *U.S.P.* 2,459,897.

A heterocyclic compound of general formula—



(X = hydrogen, alkyl, or hydroxyalkyl; Y = atoms to complete a six-membered ring), e.g. piperidine or morpholine, is used as the reducing agent, if desired in the form of a vapour, e.g. cotton fabric is impregnated with a 5% aqueous solution of silver nitrate and then exposed to the vapours of boiling morpholine. C. O. C.

Improving the Fastness of Dyeings and Prints produced with Water-soluble Dyes. Ciba Ltd. *B.P.* 619,969.

The fastness of dyeings or prints of water-soluble substantive dyes is improved by aftertreating them with an aqueous and, if desired, alkaline solution of a complex copper compound and a basic condensate of formaldehyde with a compound containing at least one $-N{:}C(N<)$ group. Thus cotton dyed with direct dyes is aftertreated with an alkaline solution of tetraamminecupric acetate and a formaldehyde–dicyandiamidine condensate. This renders the dyeing much faster to washing with soap and soda. C. O. C.

Removing Alcohol-soluble Stains from Fabric. A. W. Miller. *U.S.P.* 2,466,039.

Stains soluble in alcohol, e.g. those made by ink or iodine, are removed from fabrics without leaving any rust-like mark by first saturating the stained area with an alcohol solvent, e.g. *iso*propyl alcohol, to dissolve the stain and then saturating the stained area with a solution containing 15–30 mg. of water per 5 oz. of 10% carbolic acid. C. O. C.

Removing Shine from Fabrics. R. H. McKee. *U.S.P.* 2,459,236.

Shine may be removed from worn fabrics by treating them with a neutral aqueous solution of an alkali-metal sulphate or sulphonate of a higher organic alcohol, e.g. sodium 3:9-diethyltridecanol-6-sulphate, allowing to stand a little while, then raising the nap by a non-abrading brushing action, and finally drying. C. O. C.

Papermakers' Felts. Orr Felt & Blanket Co. *B.P.* 627,594.

Papermakers' wool felts are given longer service life if they are impregnated with approx. 5% of a cured melamine–formaldehyde resin. C. O. C.

Resin treatment of Papermakers' Felt. Orr Felt & Blanket Co. *B.P.* 626,873.

A matted papermakers' felt is impregnated with a urea-formaldehyde condensate and then heat-cured. The treated felts have much improved resistance to abrasion and chemical or bacterial action without impairment of their efficiency in removing water from paper pulp, particularly of the rate of water removal. C. O. C.

Coating Fabrics, Paper, etc. H. A. Dephillips. *B.P.* 626,627.

Coated fabrics, etc., which are impervious to water but able to transmit or absorb water vapour, are obtained by first coating the base by means of a calender with a water-impervious vinyl chloride copolymer of average mol. wt. 16,000–24,000 and then applying one or more coatings of the same polymer dissolved in a volatile solvent by knife-spreading. The spread coating may be applied either on top of the calender coating or on the other side of the fabric or paper. C. O. C.

Survey of Various Manufacturing Methods in Use by Worsted Industry for Production of Cloth, Serge, O.D. (VI, p. 80.)

Modern Trends in Piecegoods Preparation, Dyeing, and Finishing. C. N. Rabold. (VII, p. 81.)

Current Developments in Dyeing and Finishing. L. S. Thompson. (VIII, p. 82.)

XI— PAPER AND OTHER CELLULOSIC PRODUCTS

Paper, A Historical Outline. A. Latour. *Ciba Review*, (72), 2630–2639 (Feb. 1949).

Development of Papermaking. G. Schaefer. *Ciba Review*, (72), 2641–2648 (Feb. 1949).

The Paper Trade before the Invention of the Papermachine. G. Schaefer and A. Latour. *Ciba Review*, (72), 2650–2656 (Feb. 1949).

Colouring of Paper. A. Schürch. *Ciba Review*, (72), 2658–2660 (Feb. 1949).

Basic dyes are largely used for dyeing paper stock because of their brilliance, purity, and cheapness in use. Direct dyes are used for deep hues where the backwater

is required to be colourless or almost so; they have, however, very poor affinity for wood fibres. Acid dyes are used for hard-sized papers. Pigment dyes are almost exclusively used for well sized thin papers containing no wood fibres. Inorganic pigments are used where good fastness to light, water, acids, and alkalis is required, and price is not a primary consideration. Very thin paper is often coloured by being drawn through an aqueous solution of an acid or a readily soluble basic dye, if desired with a sizing agent in the solution; direct dyes are used only if great fastness to light is required. Another method is to apply a coating of the dye liquor in a machine and then festoon dry. C. O. C.

Investigation on Cellulose Reactions. VIII—An Estimation of the amount of easily Accessible Material in a Cellulose Derivative. T. Timell. *Svensk Papperstidning*, **52**, 165–167 (15th April 1949).

Triallyl cellulose, which has been isolated, is a fairly unstable product, insoluble in all solvents. The addition of iodine bromide to three allyl celluloses was shown to take place in two steps, an initial rapid conversion being followed by a slower one. Assuming that the initial conversion involves the easily accessible material of the allyl cellulose, values have been calculated for this portion in samples prepared from various celluloses which agree well with those found previously by periodic acid oxidation of the corresponding alkali cellulose. The ratio of amorphous to crystalline material thus seems to remain unchanged during the formation of fibrous ethers from alkali cellulose. S. V. S.

Influence of the Character of the Functional Groups in the Cellulose Macromolecule on the Properties of Cellulose and its Esters. Z. A. Rogovin, N. N. Shorygina, A. G. Yashunskaya, and M. G. Treyvas. *J. Appl. Chem.* (*U.S.S.R.*), **22**, 857–864 (Aug. 1949).

An investigation was made of the acetic and nitric esters of the following modified cellulose preparations formed by well known selective oxidation treatments—(*a*) "Monocarboxycellulose" made by the action of nitrogen dioxide on cellulose; this contains carboxyl groups formed by the oxidation of primary alcohol groups. (*b*) "Dialdehydocellulose" made by the action of periodic acid on cellulose; this contains aldehyde groups formed by the oxidation of 2- and 3-hydroxyl groups with rupture of the pyran ring. (*c*) "Dicarboxycellulose" made by oxidation of dialdehydocellulose by chlorous acid, the aldehyde groups being converted into carboxyls. It was found that the presence of a small proportion of aldehyde or carboxyl groups in the cellulose macromolecule has a considerable influence on the solubility properties of its acetic and nitric esters. This was thought to be the result of the formation of a number of cross-links between neighbouring chains during the esterification process. In the case of the carboxycelluloses these were regarded as ester links formed by the interaction of hydroxyl and carboxyl groups. It was expected on steric grounds that the 6-carboxyl of monocarboxycellulose would form cross-links more readily than the carboxyl groups of dicarboxycellulose, and indeed for a given carboxyl content, the reduction in solubility of the nitric and acetic esters was found to be much greater for monocarboxycellulose than for dicarboxycellulose. The importance of the configuration of the hydroxyl group participating in the cross-link was investigated by comparing monocarboxycellulose with alginic acid, the higher solubility of the esters of the latter being interpreted in terms of steric considerations of this sort. The high solubility of esters of pectic acid was considered to be due to a reduction in the probability of cross-link formation caused by the presence of methoxy groups in this polyuronic acid; in conformity with this it was found that partial methylation of monocarboxycellulose led to a considerable increase in the solubility of its esters.

A. E. S.

Preparations of Dialdehydocellulose and its Esters. A. G. Yashunskaya, N. N. Shorygina, and Z. A. Rogovin. *J. Appl. Chem.* (*U.S.S.R.*), **22**, 865–873 (Aug. 1949).

A number of dialdehydocellulose preparations were made in which the proportion of aldehyde groups varied from 3% to 91% of that theoretically possible. Nitric and acetic esters of these were prepared, and it was found, in conformity with the work of Davidson*, that the presence of a very small proportion of aldehyde groups is sufficient to cause a considerable reduction in the solubility of the esters. This was considered to be due to the formation of acetal cross-links by interaction between aldehyde and alcohol groups in neighbouring chains. Analytical results for highly oxidised products confirmed this contention; also, treatment with dilute acid caused an increase in solubility, which was considered to result from the breaking of cross-links by hydrolysis. The content of acetyl groups in fully acetylated dialdehydocellulose was found to be independent of the degree of oxidation and equal to that in cellulose triacetate. This is explicable in terms of the structure of dialdehydocellulose as a polyacetal of erythrose and glyoxal. The erythrose residue in its furanose form has only one free hydroxyl group; this accounts for one acetyl, while the remaining aldehyde group accounts for two. Simple acetals of dialdehydocellulose were made by treatment of the latter with absolute alcohol in presence of hydrogen chloride. Products of low iodine number and low alkali-solubility were obtained, but it was found that, in this case also, internal acetal formation occurred with the production of cross-links. This was confirmed by examining the product formed by treating dialdehydocellulose with hydrogen chloride in dioxan, which cannot form an acetal. A. E. S.

J. Textile Inst., **32**, T 109 (1941).

PATENTS

Paper. A. Johnson and E. C. Millatt. *B.P.* 626,518.

Calcium alginate fibres are comminuted, dispersed in water, and rendered adherent by introducing a suitable adhesive, e.g. gelatin, glue, or carboxymethyl cellulose, or by adding a swelling agent, e.g. sodium carbonate, to cause the alginic fibres to swell and become sticky in water. The bonding of the fibres in the paper made from this suspension is controlled by varying the concentration of swelling agent used. S. V. S.

Facsimile Recording Papers. F. G. Calkin and Finch Telecommunications Inc. *U.S.P.* 2,471,607.

An electrically discolourable coating for dry conductive fascimile recording paper consists in parts by weight of lead formate (1·875), titanium dioxide (5·0), zinc dust (0·31), polyvinyl acetate solution (10), and ethyl acetate (20). C. O. C.

Paper Coating. G. D. Muggleton and A. F. Piepenberg. *B.P.* 626,448.

Paper is coated with a measured film of an aqueous suspension of solids while the web is travelling in engagement with a coating roll. The film is given a heterogeneous surface pattern by the distributing roll to break up surface tension ridges, and is afterwards reworked by light engagement with a smoothing roll to obliterate the pattern marks and other irregularities before coming in contact with the paper via the coating roll. S. V. S.

Paper and other Cellulosic Sheet Materials. A. Allan, J. Horsburgh, C. A. Chester, and Wiggins Teape & Co. (1919) Ltd. *B.P.* 627,759.

Increased brightness and light-reflecting power of paper is obtained by applying to one or both sides of the paper, while passing through the dryer section and still in a wet condition (containing about 50% of water), an organic liquid, e.g. kerosene, liquid paraffin, or white spirit, immiscible with water, boiling within the range 80–350°c., and having a relatively high flash-point to minimise the risk of fire or explosion. The liquid may be added alone or as an aqueous emulsion from a bath, roll, or spray, and having completely evaporated in passing through the dryer section leaves no odour in the paper. S. V. S.

Anti-static Coatings for Cellulose Acetate Film. A. J. Daly and P. R. Hawtin. *B.P.* 627,027.

The tendency of cellulose acetate film to electrify by friction is reduced by coating with a partly saponified polyvinyl acetate containing 10–40% of the original acetyl groups and the diethylethylenediamine salt of dodecyl acid sulphate. W. G. C.

Tall Oil–Cellulose Ether Composition suitable for use in making Linoleum, etc. W. Stubblebine and Armstrong Cork Co. *U.S.P.* 2,457,847.

A composition suitable for use in linoleum manufacture and resistant to attack by alkali consists of a

filling material and a heat-cured binder obtained by treating an alkali-insoluble ethyl cellulose with more than its own weight of tall oil. C. O. C.

Stabilisers for Cellulose Esters and Ethers. W. J. Myles, J. H. Prichard, and Celanese Corpn. of America. *U.S.P.* 2,465,915.

Polyhydric alcohol esters of sulphurous acid, e.g. poly-diethyleneglycol sulphite, are colour stabilisers for cellulose esters and ethers. Ethyl cellulose may be stabilised with 1-2-propylene sulphite or ethylene sulphite. C. O. C.

Stabilised Ethyl Cellulose Moulding Composition. W. D. Paist and Celanese Corpn. of America. *U.S.P.* 2,465,472.

A moulding composition resistant to colour changes under the action of heat or light consists of ethyl cellulose, dibutyl phthalate, refined mineral oil, and 0·01–5·0% of citric acid on the weight of the ethyl cellulose. C. O. C.

Water-soluble Cellulose Ether plasticised with a *cyclo*Methylene Sulphone. G. W. Hooker, N. R. Peterson, and Dow Chemical Co. *U.S.P.* 2,471,272.

3:4-Dehydro*cyclo*tetramethylene sulphone and its 3-methyl derivative, *cyclo*tetramethylene sulphone and its 3-methyl-3-alkoxy and 3-methyl-4-alkoxy derivatives whose alkoxy groups contain 1–8 carbon atoms, are permanent non-bleeding plasticisers for water-soluble cellulose ethers. C. O. C.

Papermakers' Felts. Orr Felt & Blanket Co. (X, p. 90.)

XII— LEATHER; FURS; OTHER PROTEIN MATERIALS

Effect of Deamination and Esterification on the Reactivity of Collagen. J. H. Bowes and R. H. Kenten. *Biochem. J.*, **44**, 142–152 (1949): *Chem. Abs.*, **43**, 6258 (1949).

Treatment with nitrous acid removes all the amino groups from collagen and decreases the arginine content by about 20%, probably by the reaction of the guanidino group giving rise to $-CH_2{\cdot}NH{\cdot}CN$ and ammonia. The carboxyl groups can be esterified with dimethyl sulphate and methyl bromide, and there is no indication that any *N*-methylation occurs. Study of the construction of tannins, chrome, or formaldehyde with either untreated or deaminated and methylated collagen suggests that combination with tannins is related to the positive charge on the collagen; combination with chrome involves co-ordination of the amino and carboxyl groups of collagen with the chromium complex; and combination with formaldehyde occurs chiefly with the amino or guanidino groups. C. O. C.

PATENTS

Quinone–Resorcinol Tanning Agents. H. C. Beachell and Du Pont. *U.S.P.* 2,469,428.

A tanning composition comprises a 0·6–4 : 1 interpolymer of quinone and resorcinol and 25–150% of its weight of boric acid or an alkali borate. It yields an excellent leather of very high shrink temperature. C. O. C.

Quinone–Resorcinol Tanning Agent. J. S. Kirk and Du Pont. *U.S.P.* 2,469,437.

A tanning compound is obtained by reaction of quinone with resorcinol in presence of a solvent and an acidic polymerisation catalyst, the reaction being continued until exothermic reaction is completed, the mixture then being refluxed before the polymer is recovered. Leather produced by its use is comparable with vegetable-tanned leather in quality, and has better resistance to shrinkage when treated with hot water and to detannage by aqueous solutions at ordinary temperatures.

U.S.P. 2,469,438.

A reduction product of the above polymer is used. C. O. C.

Simultaneous Tanning with Free Formaldehyde and Melamine. W. Windus and John R. Evans & Co. *U.S.P.* 2,470,450.

White leather which does not shrink on being placed in boiling water for 5 min. is obtained by tanning the skin for at least 3 hr. in a dilute aqueous solution containing not $< 5\%$ by weight (on the wet skin) of melamine in suspension and not less than 1·5 mol. of formaldehyde per mol. of melamine. C. O. C.

XIII— RUBBER; RESINS; PLASTICS

Application of Dispersed Organic Colours in Rubbers, Vinyls, and Other Plastics. T. G. Sullivan and H. B. Watjen. *Rubber Age* (N.Y.), **65**, 182–185 (1949): *Chem. Abs.*, **43**, 5985 (1949).

A review of the use of organic colouring agents in rubber and vinyl resins, including present developments in the production of colours stable to heat and light and without tendency to migrate or bleed. Preparation of a master batch of colour by the wet method prevents agglomeration of particles and assures complete dispersion. With this method and with a protective colloid compatible with natural rubber and synthetic elastomers and plastics, a new type of colour dispersion has been developed. Possible reasons for the bleeding of some colouring agents and methods for avoiding this tendency and also fading are discussed. C. O. C.

Inorganic Pigments in Natural and Synthetic Rubber. L. H. Cohan and R. Spielman. *Ind. Eng. Chem.*, **40**, 2204–2210 (Nov. 1948).

Calcium carbonate or calcium silicate of fine particle size reinforces elastomers in a manner analogous to carbon blacks. Studies of particle size and shape, and of surface nature and crystal structure, have been made. G. L.

Polytetrafluoroethylene. W. C. Fergusson. *Plastics Inst. Trans.*, **17**, 11–24 (1949).

Polytetrafluoroethylene is probably an unbranched non-crosslinked polymer. Except for the end groups, which are unknown, its structure is probably $-[CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2]_{\text{n}}-$, the length of the chains being unknown. It is very inert chemically, has no known solvent, and does not readily flow. It is such a non-polar material that it is hard to get anything to stick to it. It may be made into a tape which is slightly translucent, but which on being heated becomes transparent and improves in physical properties. Cold-drawing greatly improves the toughness and tensile strength of the tape. Dispersions in cellulose nitrate may be used for fabricating films or for coating purposes, being heated after application to remove the cellulose nitrate. Dispersions in high-boiling liquids have also been used. There are 30 references. C. O. C.

Applications of Acrylic and Vinyl Pastes. J. A. Hetherington. *Plastics Inst. Trans.*, **17**, 25–48 (1949).

The history of vinyl pastes, mechanical mixtures of vinyl resins and plasticisers, is reviewed and their manufacture and properties are discussed. Colouring materials are best added by predispersing in 2 or 3 parts of plasticiser using a bar or ball mill. The choice of colouring matters is practically unlimited, and governed only by their stability towards heat and light and their non-bleeding characteristics. These pastes find their largest use for coating fabrics, in which application they are now competing strongly with solution-coated fabrics and latex–textile combinations and also with conventional calender-coated materials. The coating is strongly bonded to the fabric, remains flexible indefinitely, and is non-inflammable. The application is essentially simple, and requires no expensive plant. It seems probable that aqueous dispersion will continue to be used for light proofings, back-sizing of carpets, and paper-coating, but that for leathercloths the paste technique will be used. Coatings up to 20 mils thick can be applied in a single operation at speeds up to 7 yd. per min. Standard spreading equipment requires only slight modification for conversion to polyvinyl chloride paste, provision being made to raise the coating temperature to fusion point. There is no solvent and fire risk is negligible.

Acrylic pastes differ from p.v.c. pastes in that the liquid ingredient is the parent monomer, which ultimately polymerises to a solid during processing and has therefore no plasticising action on the final product. It is mainly used for dental purposes, but manufacture of methyl methacrylate sheets by direct compression-moulding of a powder–liquid paste is now being done commercially. Colouring is accomplished by ball-milling the powder with suitable pigments or with dyes dissolved in the monomer. As pigmentation is essentially confined to the surfaces of the individual grains, plain colours can be obtained only when the grain size is very small. It can be made into laminates with cloth, paper, etc., the paste being pressed

into thin sheets and allowed to gelatinise before interleaving. C. O. C.

Double Orientation and Infra-red Dichroism in Polymers. A. Elliott, E. J. Ambrose, and R. B. Temple. *Nature*, **163**, 567 (9th April 1949).

Double orientation has been detected in nylon and polyvinyl alcohol by examining the spectrum of the rolled material with polarised infra-red radiation passing through the material at an angle of 54° to the plane of the sheet. The phenomenon is most marked in nylon, where, with suitable orientation of the material, the symmetrical and antisymmetrical CH_2- stretching modes are found to have a change of dipole moment, respectively in and perpendicular to, the plane of the sheet. From quantitative measurements with polarised radiation, it appears that the direction of change of dipole moment in the N–H bond makes the same angle to the 010 plane of the nylon crystallite as does the axis of the CH_2 group which lies in the plane of the carbon chain. The angle between the C=O and N–H bonds is ~18°, and has been reduced by hydrogen-bonding forces from 39°. In hot-rolled sheets of polyvinyl alcohol, the CH_2-stretching frequencies show the same evidence of double orientation as in nylon, though to a smaller extent. Although considerable dichroism is shown by the CH_2 frequencies, the very broad O–H band shows no dichroism whatever, whether the radiation be normal to the rolled sheet or inclined so as to approximate to the direction of the extended polymer chains. H. H. H

Spherolitic Structure of Synthetic High Polymers. W. Brenschede. *Kolloid-Z.*, **114**, 35–44 (July 1949).

Polarisation-microscopic investigations of the spherolitic inclusions in polyamides and polyurethanes indicate a positive or negative character for the structures, according to the sign of the double refraction with respect to the radius of the cell element. Quantitative determination of the double refraction and observations on the thermal stability and change of sign on heating and cooling lead to the conclusion that in negative spherolites the molecular chains are preferentially oriented tangentially (specific double refraction), whereas in positive spherolites there is radial formation (from double refraction). Both effects are probably caused by a growth of the spherolites during the volume decrease of crystallisation. H. H. H.

Esterification of Polyvinyl Alcohol with Dibasic Aliphatic Acids. S. N. Ushakov, R. K. Gavurina, and P. A. Medvedeva. *J. Appl. Chem.* (*U.S.S.R.*), **21**, 1118–1125 (Nov. 1948).

The esterification of polyvinyl alcohol with adipic anhydride, or chloroanhydride, leads to cross-linked insoluble products, whereas succinic derivatives formed under similar conditions are acid esters, and readily swell or dissolve in water. A. E. S.

PATENTS

Formaldehyde – Thiol Condensates—Vulcanisation Accelerators and Agents for Improving the Adhesion of Rubber to Textiles. M. W. Harman and Monsanto Chemical Co. *U.S.P.* 2,470,555.

The products which are obtained by heating 3 mol. of a mercaptothiazole with not < 5 mol. of formaldehyde and approx. 1 mol. of ammonia in aqueous medium, which contain 5–7 mol. of formaldehyde combined with 3 mol. of mercaptothiazole, and whose S : N atomic ratio is 3 : 2, are vulcanisation accelerators. Tyre cord treated with them has improved adhesive power for rubber. C. O. C.

Amino Resins. British Resin Products, L. R. Anthony, E. M. Evans, and R. W. H. Wicking. *B.P.* 627,167.

The need for accurate pH control to avoid gelation in condensing urea or other amines with formaldehyde is obviated by condensing urea (1 mol.) with formaldehyde (> 2·25 mol.) under acidic conditions and completing the condensation by neutralising and adding sufficient urea to give the desired urea : formaldehyde ratio in the final product. The urea may be wholly or partly replaced by melamine or thiourea. E. C.

Aqueous Emulsions of Resins—Coating Compositions. W. C. Mast and U.S. Secretary of Agriculture. *U.S.P.* 2,456,295.

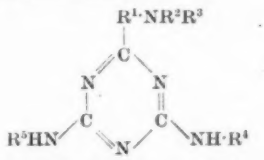
Coating compositions, whose viscosity may be varied as desired within wide limits independent of their resin content, are obtained by agitating and heating an aqueous mixture containing peptised casein (3·5–28·2 parts), a water-soluble alginate (0·25–3·75), and an acrylic ester, styrene, vinyl chloride or acetate, or vinylidene chloride (250). C. O. C.

Aqueous Emulsions of Mixed Phthalic Glyceride and Melamine–Formaldehyde Resins. D. W. Light and American Cyanamid Co. *U.S.P.* 2,471,396.

A stable oil-in-water type of emulsion is obtained by agitating a liquid containing 5–60% of phthalic glyceride resin of acid number not < 25 and 95–40% of methylol-melamine condensed with a primary monohydric alcohol in presence of an acid condensing agent with a not < 2% aqueous solution of a proteinaceous emulsifying agent, e.g. ammonium caseinate. Emulsions of this type have many uses as leather and textile finishes, paper coatings, and in inks, paints, etc. C. O. C.

Amino-Aliphatic Guanamines—Intermediates for Resins for treating Textiles. J. T. Thurston and American Cyanamid Co. *U.S.P.* 2,459,397.

Compounds of general formula—



(R^1 = an acyclic radical united to a carbon atom of the triazine ring by a carbon–carbon bond; R^2 and R^3 = hydrogen, alkyl, aryl, aralkyl, heterocyclic, acyl, or sulphonyl radicals or parts of a cyclic ring; R^4 and R^5 = hydrogen, alkyl, aryl, *cyclo*aliphatic, or heterocyclic radicals), e.g. aminoacetoguanamine, are intermediates for aminoplast resins useful in textile finishes, sizes for paper, coating compositions, etc. C. O. C.

β-Thiocarbamylthiocarboxylic Acid Derivatives—Fungicides, Vulcanisation Accelerators and Activators. B. F. Goodrich Co. *B.P.* 628,397.

β-Thiocarbamylthiocarboxylic acids obtained by treating a β-lactone with a salt of dithiocarbamic acid, e.g. $H_2N{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, obtained from ammonium dithiocarbamate and β-propiolactone, are, either as the free acids or as their multivalent metals, vulcanisation accelerators or activators, and fungicides. C. O. C.

Organic Sulphones—Stabilisers for Ethyl Cellulose. W. J. Myles and Celanese Corpn. of America. *U.S.P.* 2,465,914.

Unstable organic sulphones which yield sulphur dioxide and organic esters of sulphurous acid, e.g. α-butylene sulphone or diethyl sulphite, are stabilisers for ethyl cellulose. C. O. C.

Bis-(Trialkyl Citrate) Sulphites—Stabilisers for Cellulose Ethers. W. J. Myles and Celanese Corpn. of America. *U.S.P.* 2,465,391.

Bis-(trialkyl citrate) sulphites, obtained e.g. by treating a trialkyl citrate with thionyl chloride, stabilise cellulose ethers to heat, light, and other agencies which tend to produce colour, brittleness, and surface changes. C. O. C.

Photopolymerisation Catalyst. Du Pont. *B.P.* 622,374.

The photopolymerisation of unsaturated monomers, e.g. styrene or acrylonitrile, is performed in presence of 0·1–5·0% of an aliphatic azo compound, e.g. αα′-azodiisobutyronitrile or dimethyl αα′-azodiisobutyrate. E. C.

Chlorinated Polyvinyl Alkyl Ethers. General Aniline & Film Corpn. and C. E. Schildknecht. *B.P.* 621,910.

Polyvinyl alkyl ethers, e.g. polyvinyl *iso*propyl ether, are chlorinated at < 100° c. in presence of an inert solvent, e.g. carbon tetrachloride, and a depolymerisation inhibitor, e.g. *N*-*p*-hydroxyphenylmorpholine. The rubberlike products are suitable as finishes with good flexibility and adhesion. E. C.

Acrylic Ester–Amides and their Polymers. D. D. Reynolds, W. O. Kenyon, and Eastman Kodak Co. *U.S.P.* 2,458,420.

Compounds of general formula—

$$CH_2{:}CR^1{\cdot}CO{\cdot}O{\cdot}CH(CH_3){\cdot}CO{\cdot}NR^2R^3$$

(R^1 = hydrogen, halogen, or a cyano, alkyl, aryl, aralkyl, alkoxy, aryloxy, *cyclo*alkyl, carboxylic acyl or acyloxy, piperidyl, carboxyl, carbalkoxy, or amino group; R^1 and R^2 each = hydrogen, alkyl, or aryl), e.g. *N*-phenyl-*α*-acryloyloxypropionamide, are excellent modifying agents in cellulose ester polyvinyl acetate, and other plastic compositions. In addition they can be formed into polymers or copolymers with other unsaturated compounds to yield products suitable for use in the production of textile fibres, lacquers, films, etc. C. O. C.

Organic Polysulphides. Dunlop Rubber Co. Ltd. and M. Goldstaub. *B.P.* 618,440.

Organic polysulphides which contain terminal hydroxyl groups and of general formula $[\cdot S{\cdot}S{\cdot}X{\cdot}O{\cdot}CHR{\cdot}O{\cdot}X{\cdot}]_n$ (X = alkylene. R = hydrogen or alkyl, $n < 20$) are prepared by heating at 30–100°C. a compound of the same general formula in which $n > 20$ in intimate admixture with an acidic reagent, e.g. sulphuric acid. The products are useful as plasticisers.

B.P. 618,449.

The products of *B.P.* 618,440 (above) are esterified by heating with 10–25% of an organic dicarboxylic acid or anhydride to produce an acid ester. The products are mixed with sufficient of a bivalent metal oxide, e.g. zinc oxide or litharge, to cause hardening, on standing at room temperature, to adherent flexible masses suitable for coatings and impregnating and sealing purposes. E. C.

Inhibiting the Polymerisation of Styrene and Polymerisable Ring-chlorinated Styrenes. E. R. Erickson and Mathieson Chemical Corpn. *U.S.P.* 2,455,745.

Polymerisation of styrene and ring-chlorinated styrenes is inhibited by presence of 0·001–5·0% of a 2:5-dialkoxyquinol, e.g. 2:5-diethoxy(or -di-*n*-propoxy)quinol. *U.S.P.* 2,455,746.

A 2:5-dialkyl(or aryl)quinol, e.g. 2:5-di-*tert.*-amyl(or dibenzyl)quinol is used as the inhibitor. C. O. C.

Polymethylvinylsiloxanes. British Thomson-Houston Co. Ltd. *B.P.* 618,451.

Polymethylvinylsiloxanes with greater hardness and lower compression set on vulcanisation are prepared by hydrolysing a mixture of compounds of formula—

$(CH_3)_4SiX_2$, CH_3SiX_3, and $(CH_3)(C_2H_3)SiX_2$

(X = chlorine or alkoxyl) in such proportions as to give a product wherein the ratio of organic radicals to silicon atoms is 1·98–2·0, and 0·18–2·0% of the silicon atoms bear both a methyl and a vinyl group. Fillers and curing agents, e.g. benzoyl peroxide, may be incorporated in the products. E. C.

Polymethylsiloxanes. British Thomson-Houston Co. Ltd. *B.P.* 618,452.

Polymethylsiloxanes, prepared by hydrolysis of a mixture of compounds of formula $(CH_3)_2SiX_2$ and CH_3SiX_3 (X = chlorine or alkoxyl), are treated with strong sulphuric acid (20–30 N.) or with chlorosulphonic acid to produce gums suitable for vulcanisation with benzoyl peroxide. E. C.

Vulcanisation Accelerator. Standard Oil Development Co. *B.P.* 626,185.

Rapid vulcanisation at 240°F. of unsaturated elastomers, e.g. polychloroprene or *iso*butene–butadiene copolymers, is obtained by incorporating 0·1–6·0% of an aromatic *m*-dinitroso compound, e.g. *m*-dinitrosobenzene. E. C.

Polyesteramides for Coatings. Westinghouse Electric International Co. *B.P.* 626,145.

Polyesteramides are prepared by heating a mixture of an unsaturated dicarboxylic acid or anhydride (4·25–5·9 mol.), e.g. maleic anhydride or citraconic acid, one or more saturated (< 14 C) dicarboxylic acids (4·8–2·0 mol.) comprising > 25% succinic acid and with an average of 2·0–3·5 methylene groups per mol., an aliphatic diamine (2·1–2·65 mol.), e.g. ethylenediamine, and a glycol (5·0–6·75 mol.), e.g. ethylene glycol. E. C.

Polyethylene Terephthalate and its Early Development. D. V. N. Hardy. (VI, p. 80.)

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XIV—ANALYSIS; TESTING; APPARATUS

Cobalt Chloride Method for determining Bound Water. D. Line and H. Sheffer. *Canadian J. Res.*, **27 B**, 174–177 (March 1949).

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Spectrophotometric Determination of pH using a Mixed Indicator. I. M. Korenman and E. M. Punchik. *J. Appl. Chem.* (*U.S.S.R.*), **21**, 834–838 (Aug. 1948).

A mixture of Methyl Red and Thymol Blue is used as a pH indicator. If a definite proportion of indicator is added to a solution, the pH may be characterised by spectrophotometric absorption readings for light of wavelength 560 or 570 mμ. Alternatively, an indefinite amount of indicator may be added, and the absorption determined at 500 mμ. and at 530 or 560 mμ.; the ratio of the two readings is then characteristic of the pH. A mean error of about 0·1 is claimed. A. E. S.

Colorimetric Determination of pH in the Range 10–15. N. Konspik and O. Leberl. *Monatsh.*, **79**, 586–595 (1948): *Chem. Abs.*, **65**, 5339 (1949).

The following seven dyes are applicable even in alkali sulphide solutions—

	C.I. No.	pH Range
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Lanacyl Violet	207	11–13
Carbazole Yellow W ...	445	12–14
Chlorantine Light Blue GLN	533	13–14
Celestine Blue	900	14–15

A Lange colorimeter with two selenium cells was used, with a sensitivity of approx. 0·01–0·05 pH unit. The dye concentration was approx. 1%. Carbazole Yellow W is the least satisfactory, because it tends to flocculate. If the Lange colorimeter could be used in regions other than that of its maximum sensitivity (550–600 mμ.), a wider choice of dyes would be possible. C. O. C.

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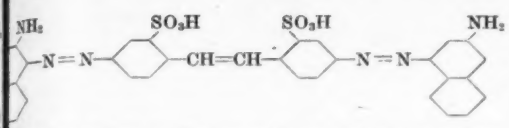
New pH Indicator for Titration of Sodium Carbonate. M. Taras. *Anal. Chem.*, **20**, 680–681 (July 1948).

The dye disodium 4:4′-bis(2-amino-1-naphthylazo)-2:2′-stilbenedisulphonate (Hessian Purple N extra, or Direct Purple) with the structure—



has a red colour in alkaline solution, undergoing a first transition at pH 4·0 with the appearance of a faint mauve colour, and a sharp change at pH 3·8 to purple, with a final change to bluish purple at pH 3·0 approx. It is thus well suited as an indicator in the titration of 0·2 or 0·5N. sodium carbonate solution or the solid salt; tests against electrometric end-points in the titration with sulphuric acid show an average deviation of 0·03% (0·2N. acid) and 0·014% (0·5N. acid). Artificial light or daylight is equally effective in detecting the first definite purple colour.

To prepare the dye, tetrazotise 9·5 g. (0·025 mol.) of 4:4′-diaminostilbene-2:2′-disulphonic acid, and couple with 14·0 g. (0·06 mol.) of β-naphthylamine dissolved in 50 ml. of glacial acetic acid and diluted to 100 ml. with water. To obtain the sodium salt, grind a weighed quantity of the dye with the calculated volume of 0·05N. sodium hydroxide in a mortar, and dilute to 0·5 or 0·1% concentration. In titrations, use 2–3 drops of 0·5% solution, or 10 drops of 0·1% solution. H. I. S.

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Sodium sulphate is converted into sulphuric acid by artificial zeolites such as Wofatit (IG) and estimated by titration. If sodium chloride is present, the latter is estimated separately by Volhard's method, and the acidity due to sulphate is obtained by difference. B. K.

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In the region of 528 mμ., where sodium carbonate gives no interference due to optical absorption, the absorptions of sodium chromate and dichromate are sufficiently different to provide the basis for a spectrophotometric determination of the ratio of their concentrations. Together with a conventional total chromium determination, this permits the estimation of both chromium compounds. The optimum wavelength varies with total chromium content. H. I. S.

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A new method is described for the determination of silica in the absence of phosphate. The silica is converted into silicomolybdic acid and precipitated as quinoline silicomolybdate from a strongly acid solution. The quinoline silicomolybdate is dissolved in excess of standard sodium hydroxide solution and back-titrated with standard acid. The method is rapid and has a smaller standard deviation than the orthodox method. W. K. R.

Rapid and Accurate Determination of Available Chlorine in Hypochlorite. V. Sinn. *Chimie analyt.*, 1947, **29**, 58: *Analyst*, **73**, 236 (April 1948).

Dissolve 19·782 g. of arsenious oxide in 120 ml. of 2·5N. sodium hydroxide, dilute to 1·5 litre, add 56 g. of sodium bromide dihydrate, neutralise to litmus with acetic acid, add a further 10% excess of acid, and dilute to 2 litres. Add the diluted hypochlorite sample (*eau de Javel* diluted 50–100 fold; bleaching powder, 7 g. to 1 litre) from a burette to 10 ml. of the 0·2N. arsenite solution, using 2–3 drops of 0·2% (sulphonated) Quinoline Yellow solution as indicator. The end-point corresponds to the sharp change from yellow–green to colourless. Chlorates do not interfere, and the accuracy is greater than that of the method of Pénot (Treadwell and Hall, *Analytical Chemistry*, **2**), which can give results with errors of 1% or more. H. I. S.

New Method for the Preparation of Adsorbents for Chromatography. D. E. Weiss. *Nature*, **162**, 372–373 (4th Sept. 1948).

Simple and versatile adsorbents, similar in behaviour to ion-exchange resins, have been prepared by adsorbing a surface-active or water-insoluble acid, e.g. fatty acids or lecithin, on to alumina, activated charcoal, or carbon black. The adsorbent acquires the properties of a "primary" adsorbate and forms, under alkaline conditions, salts which may be regarded as a "secondary" adsorbate. Elutriation by acid solutions is then possible, and the technique is no longer restricted to organic solvents. By selecting a carbon with a suitable isoelectric point, and an acid or base of the required strength, a great variety of exchange adsorbents can be prepared. Alternatively, the range of adsorbents is increased by varying the dielectric constant of the "primary" adsorbate film, and hence its surface charge. Typical curves showing the adsorption of 5-aminoacridine as a function of pH on various adsorbents are included. A. S. F.

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A system is presented for the qualitative analysis of surface-active agents of the detergent, emulsifying, and wetting types, in which some 35 chemical types are distinguished.

Tests— Unless otherwise stated, a 10 g./litre solution of the auxiliary product is used—

(1) 0·2 g. product and 0·3 g. solid sodium hydroxide are heated in a test-tube on a sand-bath at approx. 150 °C. for 1 hr. If the vapour is alkaline to litmus, it is also tested for ammonia with Nessler's reagent.

(2) 100 ml. alkaline bromine (31·2 g. bromine, 15·6 g. sodium hydroxide per litre) is added to 2 g. product dissolved in 50 ml. water. After standing 5 min. at room temperature, 50 ml. sodium hydroxide solution (300 g./litre) is added, and the whole refluxed for 2 hr., when the condenser is removed and the vapour tested with litmus-paper.

(3) 10 ml. product solution is mixed at room temperature with Resolin B (Sn) solution (10 g./litre). Turbidity indicates a cationic agent.

(4) 10 ml. similarly mixed with Solidogen BSE (IG) solution (10 g./litre). Turbidity indicates an anionic agent.

(5) 5 ml. mixed at room temperature with 10 ml. iodine solution (1·27 g., iodine 2·0 g., potassium iodide per litre). A red–brown or grey colour indicates a positive reaction.

(6) 2 g. is boiled vigorously with 40 ml. sulphuric acid (100 g./litre) under reflux for 30 min. Any separation is run off and washed 3 times with water.

(7) The final product from (6) is shaken with 20 ml. alcohol (50% by vol.), 2 drops Methyl Red are added, and titrated with 0·1N. sodium hydroxide to yellow; 2 drops phenolphthalein are added and the quantity of 0·1 N. sodium hydroxide required to obtain a red colour is determined. A positive result is > 1·5 ml.

(8) Test (6) is repeated, and the final product (decolorised with charcoal if necessary) boiled with 10 ml. Chlorantine Light Brown BRLL (Ciba) solution (0·2 g./litre). A strong coloration of the top layer is a positive result.

(9) 10 ml. product solution at pH 7 is mixed at room temp. with 10 ml. Fast Red Salt AL (20% diazotised α-aminoanthraquinone, 20 g./litre) and the resulting colour noted after 15 sec.

(10) *Guerbet's test*— 0·1 g. product is dried at 105°C., then mixed with 1 ml. fuming nitric acid, and evaporated to dryness on a sand-bath. The residue is taken up in 5 ml. 96% alcohol, 1·5 ml. 11·5 N. hydrochloric acid and 0·1 g. tin powder being added, and warmed gently, made up to 20 ml. with water, and filtered. 5 ml. of the filtrate is mixed with 5 ml. sodium nitrite solution (1 g./litre) and 5 ml. sodium acetate solution (35 g./litre). After 5 min., 5 ml. of a solution of 0·8 g. β-naphthol, 9·6 g. sodium hydroxide, and 27 g. sodium acetate per litre are added, and the colour is observed after 1–2 min. An orange–red colour indicates the presence and a yellow colour the absence of aromatic compounds.

(11) 10 ml. product solution is mixed with 10 ml. starch solution (1%) and 0·01 N. iodide added dropwise until a colour is developed.

(12) 5 ml. is mixed with 5 ml. of a solution of 174 g. ammonium thiocyanate and 2·8 g. cobalt nitrate per litre. After 2 hr. at room temperature, the colour of the liquid (not the precipitate) is noted.

(13) 10 ml. is mixed with 10 ml. of magnesium sulphate solution (20 g./litre). The effect is observed after standing for 2 hr. at room temperature.

(14) 10 ml. is similarly treated with sulphuric acid (10 g./litre).

(R^1 = hydrogen, halogen, or a cyano, alkyl, aryl, aralkyl, alkoxy, aryloxy, *cyclo*alkyl, carboxylic acyl or acyloxy, piperidyl, carboxyl, carbalkoxy, or amino group; R^1 and R^2 each = hydrogen, alkyl, or aryl), e.g. *N*-phenyl-*α*-acryloyloxypropionamide, are excellent modifying agents in cellulose ester polyvinyl acetate, and other plastic compositions. In addition they can be formed into polymers or copolymers with other unsaturated compounds to yield products suitable for use in the production of textile fibres, lacquers, films, etc. C. O. C.

Organic Polysulphides. Dunlop Rubber Co. Ltd. and M. Goldstaub. *B.P.* 618,440.

Organic polysulphides which contain terminal hydroxyl groups and of general formula $[\cdot S\cdot S\cdot X\cdot O\cdot CHR\cdot O\cdot X\cdot]_n$ (X = alkylene. R = hydrogen or alkyl, $n < 20$) are prepared by heating at 30–100°c. a compound of the same general formula in which $n > 20$ in intimate admixture with an acidic reagent, e.g. sulphuric acid. The products are useful as plasticisers.

B.P. 618,449.

The products of *B.P.* 618,440 (above) are esterified by heating with 10–25% of an organic dicarboxylic acid or anhydride to produce an acid ester. The products are mixed with sufficient of a bivalent metal oxide, e.g. zinc oxide or litharge, to cause hardening, on standing at room temperature, to adherent flexible masses suitable for coatings and impregnating and sealing purposes. E. C.

Inhibiting the Polymerisation of Styrene and Polymerisable Ring-chlorinated Styrenes. E. R. Erickson and Mathieson Chemical Corpn. *U.S.P.* 2,455,745.

Polymerisation of styrene and ring-chlorinated styrenes is inhibited by presence of 0·001–5·0% of a 2:5-dialkoxyquinol, e.g. 2:5-diethoxy(or -di-*n*-propoxy)quinol. *U.S.P.* 2,455,746.

A 2:5-dialkyl(or aryl)quinol, e.g. 2:5-di-*tert.*-amyl(or dibenzyl)quinol is used as the inhibitor. C. O. C.

Polymethylvinylsiloxanes. British Thomson-Houston Co. Ltd. *B.P.* 618,451.

Polymethylvinylsiloxanes with greater hardness and lower compression set on vulcanisation are prepared by hydrolysing a mixture of compounds of formula—

$(CH_3)_2SiX_2$, CH_3SiX_3, and $(CH_3)(C_2H_3)SiX_2$

(X = chlorine or alkoxyl) in such proportions as to give a product wherein the ratio of organic radicals to silicon atoms is 1·98–2·0, and 0·18–2·0% of the silicon atoms bear both a methyl and a vinyl group. Fillers and curing agents, e.g. benzoyl peroxide, may be incorporated in the products. E. C.

Polymethylsiloxanes. British Thomson-Houston Co. Ltd. *B.P.* 618,452.

Polymethylsiloxanes, prepared by hydrolysis of a mixture of compounds of formula $(CH_3)_2SiX_2$ and CH_3SiX_3 (X = chlorine or alkoxyl), are treated with strong sulphuric acid (20–30 N.) or with chlorosulphonic acid to produce gums suitable for vulcanisation with benzoyl peroxide. E. C.

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XIV—ANALYSIS; TESTING; APPARATUS

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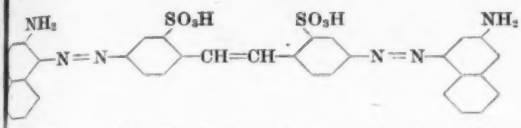

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(8) Test (6) is repeated, and the final product (decolorised with charcoal if necessary) boiled with 10 ml. Chlorantine Light Brown BRLL (Ciba) solution (0·2 g./litre). A strong coloration of the top layer is a positive result.

(9) 10 ml. product solution at pH 7 is mixed at room temp. with 10 ml. Fast Red Salt AL (20% diazotised α-aminoanthraquinone, 20 g./litre) and the resulting colour noted after 15 sec.

(10) *Guerbet's test*— 0·1 g. product is dried at 105°c., then mixed with 1 ml. fuming nitric acid, and evaporated to dryness on a sand-bath. The residue is taken up in 5 ml. 96% alcohol, 1·5 ml. 11·5N. hydrochloric acid and 0·1 g. tin powder being added, and warmed gently, made up to 20 ml. with water, and filtered. 5 ml. of the filtrate is mixed with 5 ml. sodium nitrite solution (1 g./litre) and 5 ml. sodium acetate solution (35 g./litre). After 5 min., 5 ml. of a solution of 0·8 g. β-naphthol, 9·6 g. sodium hydroxide, and 27 g. sodium acetate per litre are added, and the colour is observed after 1–2 min. An orange–red colour indicates the presence and a yellow colour the absence of aromatic compounds.

(11) 10 ml. product solution is mixed with 10 ml. starch solution (1%) and 0·01N. iodide added dropwise until a colour is developed.

(12) 5 ml. is mixed with 5 ml. of a solution of 174 g. ammonium thiocyanate and 2·8 g. cobalt nitrate per litre. After 2 hr. at room temperature, the colour of the liquid (not the precipitate) is noted.

(13) 10 ml. is mixed with 10 ml. of magnesium sulphate solution (20 g./litre). The effect is observed after standing for 2 hr. at room temperature.

(14) 10 ml. is similarly treated with sulphuric acid (10 g./litre).

(15) 10 ml. is made just acid to phenolphthalein, 0·3 g. sodium chloride, 3 drops of sulphomolybdate reagent (10 g. ammonium molybdate, 300 ml. sulphuric acid (50% by vol.) per litre) and a strip of tin foil are added, shaken, and allowed to stand for 30 min.

(16) 5 g. product after steaming off any solvents present is refluxed for 2 hr. with 60 ml. sodium hydroxide solution (300 g./litre) and then distilled, and the distillate examined for alcohols.

(17) The product is heated in an open test-tube at 110°C. for 24 hr., then examined for solubility in boiling water.

(18) As test (17), except that the product is first adjusted to pH 5 with 0·1 N. hydrochloric acid.

(19) 10 ml. solution is mixed with 10 ml. of sodium hydroxide solution (50 g./litre) at room temperature and the effect observed immediately.

(20) *Biuret test*— 10 ml. solution is mixed with 10 ml. sodium hydroxide solution (10 g./litre) and 1·5 ml. copper sulphate solution (3 g./litre). A violet coloration on warming indicates a positive reaction.

ANALYTICAL PROCEDURE

Test and Result	Further Procedure or Inference
(1) No alkaline vapours	Scheme A
Alkaline vapours—	
(Nessler) Negative	Scheme B
Positive—	
(2) No alkaline vapours	Scheme A
Alkaline vapours	Scheme B
Scheme A	
(3) Turbid—	
(4) Clear	Sulphonium compounds
Clear—	
(4) Clear	GROUP A II
Turbid	GROUP A III
GROUP A II	
(5) Negative	*Subgroup* A II *a*
Positive	*Subgroup* A II *b*
Subgroup A II *a*	
(6) Clear	Short-chain ethers, esters, alcohols, aldehydes, acids and thioethers
Separation—	
(7) Positive	Fatty acid monoesters of polyhydric alcohols
Subgroup A II *b*	
(9) Orange to brown	Polyethylene oxide–alkylnaphthols
Weakly coloured—	
(10) Orange to red	Polyethylene oxide–alkyphenols
Yellow—	
(6) (7) Positive	Polyethylene oxide–fatty acid esters
Clear or turbid after cooling—	
(11) Blue	Polyethylene oxide–short chain ($< C_{10}$) aliphatic alcohols
Red	Polyethylene oxide–long-chain aliphatic alcohols
GROUP A III	
(9) Red-brown	Ricinoleylcresol compounds
Orange-brown	Alkylnaphthalene-sulphonates
Weakly coloured—	
(6) No separation—	
Turbid	*Subgroup* A III *d*
Clear	*Subgroup* A III *e*
Separation—	
Emulsifies on washing	*Subgroup* A III *c*
(7) Negative	*Subgroup* A III *a*
Positive	*Sub-group* A III *b*
Subgroup A III *a*	
(5) Positive—	
(12) Blue	Aliphatic alcohol–polyethylene oxide sulphates
Negative—	
(12) Violet—	
(13) Clear	Alkyl sulphates
Turbid—	
(15) Negative	Sulphated oleyl-acetate
Positive	Alkyl phosphates
Subgroup A III *b*	
(14) Clear—	
(16) Negative—	
(18) Soluble	Fatty acid esters of ethionic acid
Insoluble	Highly sulphated fats
(16) Positive—	
(11) Blue	Sulphonates of di-octyl succinate
Red	Ricinoleyl alkyl ester sulphates
Turbid—	
(17) Insoluble	Polymerised ricinoleyl sulphates
Soluble—	
(19) Clear or slightly turbid	Low-sulphated fats
Very turbid	Soap
Subgroup A III *c*	
(16) Positive	Ricinoleylalkyl ester sulphonates
Negative—	
(10) Orange to red	Alkarylsulphonates
Yellow	Alkylsulphonates
Subgroup A III *d*	
(13) Clear	Alkyl sulphates
Turbid—	
(10) Orange to red	Alkarysulphonates
Yellow	Alkysulphonates
Subgroup A III *e*	
(10) Orange to red	Alkarylsulphonates
Yellow	Alkylsulphonates
Scheme B	
(3) Turbid—	
(4) Clear	GROUP B I
Clear—	
(4) Clear	GROUP B II
Turbid	GROUP B III
GROUP B I	
(11) Blue–violet	Short-chain cation-active amines
Yellow to red	Long-chain cation-active amines
GROUP B II	
(5) Negative—	
(12) Violet	Short-chain amino-polycarboxylic acids amines, or amides
Positive—	
(12) Blue—	
(6) Clear	Amino–polyethylene oxides
Separation	Fatty acid amide-polyethylene oxides
GROUP B III	
(9) Orange to brown	Alkylnaphthalene-sulphonates
Weakly coloured or yellow	
(6) No separation but turbid	*Subgroup* B III *f*
Separation—	
Emulsifies on washing	Lissapol LS (ICI)
(8) Negative—	
(7) Negative	*Subgroup* B III *a*
Positive	*Subgroup* B III *c*
(8) Positive—	
(7) Negative	Anion-active amino compounds
Positive	Alkylamido sulphates
Subgroup B III *a*	
(13) Turbid—	
(14) Turbid—	
(9) Yellow	Albatex PO
Clear—	
(14) Clear	Anion-active amino compounds (analyse as *Subgroup* A III *a*)
Subgroup B III *c*	
(20) Positive	Fatty acid–albumin condensates
Negative	Anion-active amino compounds (analyse as *Subgroup* A III *b*)
Subgroup B III *f*	
(9) Yellow	Ultravon W
Weakly coloured	Alkyl amido sulphonates

W. K. R.

Improved Technique for Measurement of the Dispersing Powers of Detergents. F. D. Snell and I. Reich. *J.S.C.I.*, **68**, 98–100 (March 1949).

A method for measuring the dispersing power of detergent solutions (Snell, *Ind Eng. Chem.*, **25**, 162 (1933)) has been simplified. An artificial soil composed of burnt umber lightly oiled with a mixture of vegetable oil, mineral oil, and oleic acid is agitated with the detergent solution and allowed to stand in a Nessler tube for 2 hr. A sample of the suspension is then withdrawn, and its turbidity determined in a modified electric turbidimeter. The results are expressed as 100 times the reciprocal of the length needed just to obscure the filament. The relationship between this value and the concentration of suspended soil is shown to be linear. With cloudy detergent solutions the value is corrected by subtracting the reciprocal reading of the detergent solution from that of the suspension. Typical

dispersing power values for various types of detergent are listed, those for soaps being considerably higher than those of the synthetic detergents tested. W. K. R.

Detergency Evaluation. J. Powney and A. J. Feuell. *Research*, **2**, 331–333 (July 1949).

The use of chopped fibres instead of fabric for evaluating the efficiency of different detergents has several advantages, one being that a reliable result can be obtained by one photometric observation as against a minimum of eight if fabric is used, another that variations in the degree of soiling of individual fibres are averaged out by the very effective randomisation achieved in both the soiling and the washing stages, and reproducibility is good, being ± 5% or better. The chopped fibres are soiled by working them with a solution of the soil in an open dish and well mixing them after drying. The washing test is done in a beaker, mechanical action being supplied by a close fitting, dished, perforated brass plunger reciprocating in the beaker. C. O. C.

Detergent Action. O. C. Bacon and J. E. Smith. *Ind. Eng. Chem.*, **40**, 2361–2370 (Dec. 1948).

Variables studied were detergent concentration, mechanical work, and time required to remove soil in a washing process. The mechanical work performed was controlled by varying the speed of the washing machine and the number and mass of balls employed in it. An equation relating the variables with detergent action has been derived, and a method of calculating the % coloured soil removal from reflectance data is presented. The principles established provide a basis for development of a comprehensive method for evaluation of detergents. G. L.

Measurement of Rates of Spread of Solutions of Surface-active Agents. J. Hypia. *Anal. Chem.*, **20**, 1039–1043 (Nov. 1948).

An apparatus is described in which a fixed volume of solution is delivered in a uniform manner, using a standard mercury head, through a pipette to the surface studied. The same mercury head, upon release, actuates a relay which sets in motion a device for intermittently photographing the drop at 2·5- or 5-sec. intervals. From the resulting photographs, drop area–time graphs, and hence rates of spreading, may be obtained. The apparatus is applicable to glass and other surfaces, including suitably stretched textiles. H. I. S.

Evaluation of Powdered Tragacanth—Determination of Viscosity of Mucilage. Society of Public Analysts Analytical Methods Committee, Tragacanth Sub-committee Report No. 1. *Analyst*, **73**, 368–377 (July 1948).

The falling sphere method of determining mucilage viscosity is rejected because of non-reproducibility ensuing from the requisite high concentrations, as well as opacity difficulties. The U tube viscometer method is rejected because of non-reproducibility arising from the non-Newtonian behaviour, which makes standard capillary bores necessary; homogenisation of mucilages by means of domestic cream-making equipment leads to unpredictable variations in viscosity. The Redwood viscometer method gives reasonably reproducible results with independent observers, and is adapted as the basis of a recommended procedure in which the concentration C_g of gum (on a water-free basis) which gives an efflux time of exactly 100 sec. for 50 ml. in a Redwood No. 1 viscometer at 20°c. is determined by interpolation from the linear plot of logarithm of concentration C_E against efflux time E. This plot has a constant slope of 0·002 (standard deviation ± 0·0006) for E values of 75–125 sec., and thus only one experimental determination is necessary in order to evaluate C_g.

Procedure— Determine the moisture content by drying about 1 g. of gum sample in an open dish to constant weight in a steam-heated oven. Place a suitable weighed quantity of (undried) powdered gum in a dry 500 ml. conical flask, add 5 ml. of 95% alcohol, and completely wet the powder and disperse it evenly over the inner surface of the flask. Add 195 ml. of cold distilled water as quickly as possible, shake, and then reflux for 1 hr. with the flask immersed in vigorously boiling water extending about 1 in. above the level of the mucilage surface; swirl gently at 15-min. intervals without removal from the bath. Then remove the flask stopper, and allow to cool naturally to room temperature. After 24 hr., determine the efflux time E sec. of 50 ml. in a Redwood No. 1 viscometer at 20°c., taking the mean of 6 readings. Correct to a water efflux time of 27 sec. by multiplying the result by $27/x$, where x is the efflux time of 50 ml. of water under the same conditions in the same instrument. If E is not between 75 to 125 sec., repeat with suitably altered concentration, using a freshly prepared mucilage and not a diluted one. Calculate the % concentration C_g of dry gum corresponding to $E = 100$ sec. from the equation—

$$C_g = \text{antilog } [\log C_E - 0{\cdot}002E + 0{\cdot}2]$$

where C_E is the concentration of dry gum corresponding to E (corrected). H. I. S.

Evaluation of Flake Tragacanth. Society of Public Analysts Analytical Methods Committee, Tragacanth Sub-committee 2nd Report. *Analyst*, **74**, 2–6 (Jan. 1949).

Viscosity is determined by the method described in Report No. 1 (*Analyst*, **173**, 368–377 (July 1948)) for the evaluation of powdered tragacanth, but it cannot be regarded as a measure of suspending power, since mucilages prepared from different gums and having the same efflux time in the Redwood viscometer vary considerably in their suspending power for bismuth carbonate. It is recommended, therefore, that for the latter purpose a test should be made with the concentration of tragacanth normally employed and using all the materials it is desired to suspend. The % of ash is apparently unrelated to the quality of the tragacanth, and the method of determination of sulphated ash gave results of better concordance than by direct ignition. The determination of volatile acidity is recommended as of value in detecting adulteration of tragacanth with Karaya gum and with gum Ghatti; details of both the above estimations are included. H. H. H.

Assessment of Thickening Agents. W. Jülicher. *Melliand Textilber.*, **30**, 308–311 (July 1949).

The purity of thickening agents for printing can be assessed by centrifuging a weak solution and testing the centrifuged residue for viscosity. B. K.

Colorimetric Determination of Some Nitrophenolic Proofing Agents in Felt. J. G. Norvall and C. Kenyon. *Analyst*, **73**, 551–554 (Oct. 1948).

Mixtures of *p*-nitrophenol and either 2:4-dinitro-*α*-naphthol or 4:6-dinitro-*o*-cresol, impregnated on felt to afford proofing against bacteria and fungi, are determinable with an accuracy of 3% by extracting from the felt with hot water, removing wool acids from the extract with lead acetate, extracting the nitro compounds from the liquid with ether, separating the two components by chromatography on alumina and elution with hot water, and finally determining the *p*-nitrophenol absorptiometrically by reduction and application of the Indophenol-Blue reaction and the dinitro compound similarly by reduction and reaction of the amino product with ferric chloride. H. I. S.

Quantitative Determination of Synthetic Resins in the Fibre. W. Ernst and M. Sorkin. *Textil-Rund.*, **4**, 237–247 (July 1949).

A review of previous proposals is followed by an account of experimental work and finally by details of a proposed system for the qualitative and quantitative analysis on the fibre of formaldehyde resins or their mixtures with other finishing agents. C. O. C.

Qualitative Reactions of Primary Arylamines. S. I. Burmistrov. *J. Anal. Chem.* (*U.S.S.R.*), **1**, 265–271 (1946): *Chem. Abs.*, **43**, 5344 (1949).

Five reactions for identifying primary arylamines are described—(1) Formation of Schiff-type bases with dimethylaminobenzaldehyde; these compounds yield coloured salts with acids. (2) Diazotisation followed by coupling with *α*-naphthol or phenol. (3) Coupling with a nitrophenyldiazonium salt and developing colour in gaseous hydrogen chloride. (4) Formation of quinobromoimines and quinobromodiimines by action of bromine. (5) Test for *o*-methylacylamines. For these tests a solution containing 1–2 mg. of acylamine per ml. of a volatile solvent, e.g. ether, benzene, chloroform, ethylacetate, or dimethylketone, is applied on a strip of filter-paper. After the solution has evaporated the reagent is applied as a 2 mg./ml. benzene solution. After the paper has dried, it

is exposed to a gas, e.g. ammonia, hydrogen chloride, bromine, or alkyl nitrite. The specific reactions of 58 compounds are listed. C. O. C.

Qualitative Tests for Azotols (Naphtol AS). S. I. Burmistrov. *J. Anal. Chem.* (*U.S.S.R.*), **1**, 315–318 (1946): *Chem. Abs.*, **43**, 5344 (1949).

The method of the preceding abstract is extended to the Naphtol AS series. Naphtol AS–BS is identified by reducing it to the corresponding acylamine and then testing for a diazo reaction. Naphtol AS–GR and AS–SR are distinguished from arylamides of 2:3-hydroxynaphthoic acid by the colour of their coupling products. Other Naphtols are hydrolysed in alkaline alcoholic solution to yield arylamines which are then identified by their specific reactions. The specific colour reactions of 13 Naphtols are listed. C. O. C.

Amperometric Titration with Diazotised Aromatic Amines. R. M. Elofson and P. A. Mecherly. *Anal. Chem.*, **21**, 565–567 (May 1949).

The amperometric titration of a coupler such as a pyrazolone or a naphthol with diazotised amines in well buffered solutions is described. Diazotised *p*-toluidine has been found the most generally useful of the various diazotised amines. The method depends upon the amperometric measurement of the excess diazo compound present after the end-point is reached, and a dropping mercury electrode against a saturated calomel electrode with an applied potential of 0·2–0·3 v. is used. The chief advantage of the new over the optical method lies in the fact that it is not necessary to arrange for the formation of soluble dyes, which makes the process more versatile. Techniques are given for the estimation of diazotised amines and of couplers. The importance of temperature and pH control is emphasised. H. H. H.

Reaction of Nitrous Acid with Alcoholic *α*-Naphthylamine Hydrochloride and its Application to the Absorptiometric Determination of Nitrites. C. A. Parker. *Analyst*, **74**, 112–118 (Feb. 1949).

The colorimetric reaction between nitrous acid and an aqueous-alcoholic solution of *α*-napthylamine hydrochloride has been investigated with respect to the effects of acid normality, alcohol concentration, and temperature upon the reaction velocity and maximum colour intensity. Some observations are included with regard to the mechanism of the reaction. From the results obtained, a sensitive and accurate absorptiometric method for the estimation of nitrite has been developed, which has advantages of rapidity, colour stability, and reproducibility; few ions cause serious interference, and the dye formed obeys Beer's law over a wide concentration range. H. H. H.

Determination of *p*-Phenylenediamine by Diazotisation. M. D. Zhorina. *Zavodskaya Lab.*, **13**, 1180, 1181 (1947): *Chem. Abs.*, **43**, 4185 (1949).

Dilute a 4-g. sample in water containing 5 ml. concentrated hydrochloric acid to 500 ml., treat a 50-ml. aliquot with 5 ml. concentrated hydrochloric acid and 35 ml. acetic acid, cool to 5°c., dilute to 200–300 ml., and titrate with 0·1N. sodium nitrite using starch–iodide paper as indicator. C. O. C.

Determination of Diphenyl Carbonate. J. Goldenson and S. Sass. *Anal. Chem.*, **20**, 730–732 (Aug. 1948).

Three methods are described for estimating diphenyl carbonate in cloth, in which it is used as a miticide and larvicide, viz. (I) ultra-violet absorptiometry of the compound itself or its phenolic decomposition product, (II) quantitative bromination (to 2:4:6-tribromophenol) of the phenol produced by alkali treatment, and (III) absorptiometry of the blue indophenol colour given by the phenol decomposition product and 2:6-dibromoquinonechloroimine. H. I. S.

Colorimetric Determination of Certain Dinitro Aromatics in Presence of Corresponding Mononitro Compounds. F. L. English. *Anal. Chem.*, **20**, 745–746 (Aug. 1948).

Small amounts of dinitro-benzene, -chlorobenzene, -naphthalene, -toluene, and -xylene in their mononitro derivatives are determined with a photoelectric absorptiometer by making use of the colour obtained when dilute alcoholic sodium hydroxide (specially prepared from sodium monoxide) is added to an acetone solution of the sample. Similarly, dinitrocresol in mononitrotoluene is determined by means of the colour given by sodium hydroxide in aqueous solution. Determinations require 10–15 min., and are reproducible within ± 3%. H. I. S.

Detection of Methylpyridine and Aniline in Pyridine. T. Ogata and T. Isa. *Bull. Inst. Phys. Chem. Research* (Tokyo), **21**, 621–630 (1942): *Chem. Abs.*, **43**, 1689 (1949).

The purity of commercial pyridine can be estimated from the weight of the fraction that distils at 100–115°c. and from the weight of the methyl iodide derivative that can be prepared from it. The principal impurity of pyridine is 2-methylpyridine, whose methyl iodide derivative gives characteristic colour reactions with $C_6H_5{\cdot}N{:}CH{\cdot}NH{\cdot}C_6H_5$, p-$(CH_3)_2N{\cdot}C_6H_4{\cdot}CHO$, p-$(CH_3)_2N{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CHO$, p-$(C_2H_5)_2N{\cdot}C_6H_4{\cdot}NO$, 2-anilinovinylquinoline methiodide, and chloroform or chloral hydrate. Aniline and other impurities are detected by reaction with the 2-$CH_3{\cdot}CO{\cdot}N{\cdot}(C_6H_5)[CH{:}CH]_3$– derivative of benzoxazole methiodide, which gives a violet compound. C. O. C.

Testing the Purity of Pyridine. T. Ogata and H. Takida. *Bull. Inst. Phys. Chem. Research* (Tokyo), **21**, 855–859 (1942): *Chem. Abs.*, **43**, 1689 (1949).

Use of potassium permanganate is not as good for detecting the presence of reducing agents as use of melamine (cf. preceding abstract). When *α*-picoline is present, it is better to determine pyridine gravimetrically by weighing the methyl iodide derivative than by titrating with N. hydrochloric acid. C. O. C.

Acidimetric Titration of Dark-coloured Solutions. W. Hirsch. *Analyst*, **73**, 160 (March 1948).

To a dark-coloured acid solution in a glass-stoppered vessel add a few drops of dilute lead acetate solution and a few ml. of a 0·005% solution of dithizone in chloroform, carbon tetrachloride, ethyl acetate, amyl alcohol, benzene, or any solvent in which the dark colour is insoluble. Titrate with N. or 0·1 N. sodium hydroxide, shaking after each addition. The end-point corresponds to the change from the green dithizone to the red lead-dithizone compound; it occurs at about the same pH as the Methyl Orange end-point, and therefore this method is not applicable to weak acids. H. I. S.

Volumetric Titrations in Strongly Coloured Solutions. M. Brut. *Chimie analyt.*, **29**, 85 (1947): *Analyst*, **73**, 236 (April 1948).

Add to the coloured solution another of complementary colour which does not affect the chemical reaction, but produces a grey tint which does not obscure the colour change to be observed. Thus 10% (wt./vol.) cobalt sulphate solution neutralises the green colours in (i) determining chromate by reduction with ferrous sulphate and back-titrating excess with permanganate, (ii) titrating chromic acid solutions containing considerable nickel, and (iii) determining manganese by oxidising to permanganate reducing with ferrous sulphate, and back-titrating excess of ferrous ion, in the presence of considerable nickel; here the cobalt is added before the oxidation. Conversely, solutions coloured by cobalt salts may be treated with nickel sulphate to neutralise the colour. H. I. S.

Identification of Certain Coal-tar Dyes used in Cosmetics. K. A. Freeman. *Proc. Sci. Sect. Toilet Goods Assocn.*, **11**, 20–24 (1949): *Chem. Abs.*, **43**, 6364 (1949).

A complete method is given for separating the 16 certifiable paste colours found in Koch's Group VII (cf. *Chem. Abs.*, **37**, 5498 (1937)) from the products in which they are used and from one another. Identification of the dyes is made by comparison with standard absorption curves using a General Electric electrospectrophotometer. C. O. C.

Outline of Qualitative Dye Analysis. W. E. Mathewson. *Amer. Dyestuff Rep.*, **37**, 709–725 (1st Nov. 1948).

The system depends on the extraction of a dye from its aqueous solution by organic liquids in the presence of acid, alkali, or salt and is particularly useful in separating dye mixtures. The solvents used are *iso*amyl alcohol, ethyl ether, petroleum ether and aniline or *n*-butylamine. The unknown dye solution (0·01–0·1%) or the extract from a dyed pattern is shaken with an equal vol. of 1 : 1 *iso*amyl alcohol–petroleum ether and half its vol. of conc. hydrochloric acid. If a precipitate is formed, the dye acids are filtered, moistened with N. potassium hydroxide,

and dissolved in water, slightly acidified, and fractionated with 1 : 2 *n*-butylamine–*iso*amyl alcohol. The mixed-solvent filtrate is allowed to separate, and the lower layer drawn into a second separating funnel containing 1 : 1 *iso*amyl alcohol–petroleum ether. The solvent layers are washed with 4N. hydrochloric acid, the fractionation being continued if necessary. The final solvent layer is further fractionated with dilute hydrochloric acid of decreasing strength and with water, whilst the final acidic aqueous solution is extracted with *iso*amyl alcohol. From the results of these tests the separated dyes or fractions are allocated between ten groups, the members of which are further separated and in some cases identified by means of a series of solvent partition tests. Separated dyes are further identified by the effect of oxidation by bromine, and by noting the colour change when hydrochloric acid, sodium hydroxide, and sodium hydrosulphite are added to the aqueous dye solution, the colour of the solution of the dye in conc. sulphuric acid, and the change in colour when divanadyl trisulphate is added thereto. The analytical schemes cover the separation of some 200 dyes (*Colour Index* numbers quoted) of the basic, direct, acid, and chrome classes, and tables give the colour reactions of the individual dyes. W. K. R.

An X-ray Method for the Determination of the Ratio of Crystalline to Amorphous Substance in Cellulose Fibres. W. Kast and L. Flaschner. *Kolloid-Z.*, **111**, 6–15 (Oct. 1948); 132 (Nov. 1948).

A method is described for the estimation from X-ray diagrams of the proportions of crystalline and amorphous substance in cellulose fibres. The treatment is largely mathematical and is illustrated by three diagrams. There are tables of data for cuprammonium and Bemberg rayon. Data corrections are given in the second communication. H. H. H.

Determination of the Specific Gravity of Pigments. W. W. Ewing and R. N. Rhoda. *Anal. Chem.*, **20**, 743–745 (Aug. 1948).

The Archimedes displacement method is used, with an aqueous wetting agent solution as immersion liquid, for inorganic hydrophilic pigments. For hydrophobic pigments, a different wetting agent, perhaps even an oil-soluble agent in an organic solvent, would be necessary. Adsorption of wetting agent may cause appreciable errors in results, especially with very finely divided pigments, if the density of the adsorbed layer is not approx. equal to that of the surrounding solution.

Procedure— Weigh, in air, about 10 g. of dry pigment (W_1) in a tared small test-tube containing a glass stirrer and suspended by a platinum wire. Cover the solid with 0·2% aqueous solution of wetting agent Hornkem No. 1 (sp. gr. 0·9973 at 25°c.), stir to a uniform slurry, centrifuge until the solid is well packed at the bottom of the tube, and then reweigh (W_2) whilst tube and contents are completely immersed in the wetting agent solution contained in a Dewar vessel at 25 ± 0·01°c. Then, allowing for the weight of the glassware in air and in the liquid, and correcting all weights to vacuum, the required sp. gr. is given by $0{\cdot}9973 \times W_1/(W_1 - W_2)$. Reproducibility is about ± 0·05%. H. I. S.

Physical and Chemical Measurements of Cotton and Linen Materials. K. Huber. *Textil-Rund.*, **4**, 310–328 (Sept. 1949).

Viscosity measurements of cotton and linen which have been subjected to chemical treatments, solubility of cellulose in Schweizer's reagent, fluidity numbers, estimation of degree of polymerisation, and the relationship between viscosity and tensile strength are discussed. B. K.

Microbiological Degradation of Cotton Fabrics. R. G. H. Siu and W. L. White. ORR 124/49* (PB 22,339).

Experimental results are described on the isolation and identification of fungi from deteriorated fabrics, the organisms, strains, and activities being tabulated. Brief details of several usable methods for breeding and testing cellulolytic micro-organisms are given under the headings—standard procurement test method, Petri dish liquid method, the shaker-flask method, tube culture method, and sand culture method. Methods for investigating the influence of ultra-violet radiation, atmospheric oxygen, humidity, and temperature on the rate and degree of biological degradation of cotton are described. Work on enzymes and the use of resin impregnation for preventing microbiological attack in cotton are also described. C. O. C.

* Photocopies available from T.I.D.U., Board of Trade, 40 Cadogan Square, London S.W.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.—see J.S.D.C., **66**, p. 53 (Jan. 1950).

Effect of Preliminary Hydrolysis on the Determination of Lignin in Jute. A. P. Sen Gupta and H. J. Callow. *J. Textile Inst.*, **40**, T650–T655 (Sept. 1949).

In the determination of lignin in jute it has been suggested that a pretreatment with dilute acid should be given to remove pentoses, which otherwise may cause a high value for the lignin to be obtained. It has been found that a small proportion of the lignin is removed by this treatment, and it is concluded that its omission leads to more accurate results. W. J. M.

Yellowing of Bleached Jute. P. B. Sarkar. *Current Sci.* (India), **16**, 287 (1947): *Chem. Abs.*, **43**, 6422 (1949).

That presence of moisture is essential for the discoloration of delignified jute is indicated by its remaining unchanged in colour when stored over fused calcium chloride in a desiccator, becoming very slightly brown over concentrated sulphuric acid and normally yellowed over a saturated solution of ammonium chloride. It also turns appreciably yellow when stored in the dark. C. O. C.

Coir Fibre— Structure and Identification of Damage. S. R. Sengupta, B. B. L. Saxena, and A. N. Mukerjee. *J. Sci. Ind. Research* (India), **8 B**, 61–65 (1949): *Chem. Abs.*, **43**, 5595 (1949).

Fresh coir fibres are composed of a rudimentary protoxylem enclosed by a thick sclerenchymatous sheath. During retting the protoxylem disintegrates. The cell wall is thick, with a narrow air-containing lumen. It shows secondary thickening and reticulate thickening of the cells. On maceration the surface shows silicified stigmata cells. The main components of the cell wall are cellulose and lignin. Treatment of teased material with 1% Safranine solution for 3 min. and washing on a slide stains normal fibres pink or violet, tendered fibres deep red. Chemical damage may be identified by swelling the fibres on a slide with 1–2 drops of zinc chloroiodide solution for 1–9 min. over a steam-bath, and microscopic examination of damaged cells shows: HCl—Regular wavy curling on entire length; cuticle is intact. HNO_3— Cuticle is ruptured at intervals with slight swelling and sharp segmentation. H_2SO_4— Considerable swelling of cells occurs, forming bubbles with constrictions in between, slight curling, and occasional pigmentation. Caustic alkali— No curling; bubble formation with central lumen inside. Oxidation (peroxide, bleaches, weathering)— The entire secondary wall turns blue at once. H_2O_2— Formation of small bubbles in addition. Damage by bacteria or fungi is not detectable by zinc chloroiodide swelling; the microscopic cross-section shows irregular, indented hollow zones. Bacteria cause indentations on the surface of the fibre in addition to this. C. O. C.

Electron Microscopic Examination of Wool containing Polymer. E. H. Mercer. *J. Textile Inst.*, **40**, T 629–T 639 (Sept. 1949).

Optical and electron micrographs of wool containing polymethacrylic acid and retted with trypsin show the fibrous cortical cells of wool. The electron micrographs in addition indicate the presence of the polymer. The polymer seems to have been deposited in the extrafibrillar regions in the fibres. In acid and neutral solutions the polymer is in a coherent form, and in alkaline solutions it ionises; this explains the behaviour of treated wool in such solutions. W. J. M.

Hydroxylysine and Lysine in Wool. W. R. Middlebrook. *Nature*, **164**, 321 (20th Aug. 1949).

A chromatographic method for estimating the lysine content of wool has been developed. The lysine content was found to be 3·38% and the hydroxylysine 0·18%. W. J. M.

Detection of Alkali Damage in Wool. R. Genet. *Textil-Rund.*, **4**, 351–364 (Oct. 1949).

A review of published work dealing with theoretical aspects of alkali damage to wool, the relationship between chemical and physical properties of alkali-damaged wool,

and methods of estimating them. Estimation of tensile strength and extensibility gives a good indication of the possible commercial uses of alkali-damaged wool. 61 references to the literature are given. B. K.

Simplified Method for the Estimation of the Alkali Solubility of Wool. H. Zahn. *Textil-Praxis*, **4**, 70–71 (Feb. 1949).

The alkali solubility of wool indicates the amount of damage due to bleaching, carbonising, and discharge printing, but is not proportional to the extent of mechanical damage caused by treatment of wool with alkalis or enzymes. Alkali solubility is readily estimated by treatment with 0·02 N. caustic soda for 1 hr. on a boiling water-bath. B. K.

Estimation of 2:4-Dinitronaphthol and Martius Yellow in Woollen Fabrics. C. N. Tewari, S. C. D. Gupta, and B. C. Bera. *J.S.C.I.*, **68**, 126–127 (April 1949).

Two methods are described— (*a*) The dye is extracted with distilled water in a Soxhlet and estimated spectrophotometrically at a wavelength of 500 mμ. (*b*) The dye is extracted with 95–96% alcohol in a Soxhlet, and the alcohol evaporated. The dye is estimated by reducing the nitro groups with excess titanous chloride in acid and back-titrating the excess reducing agent. W. J. M.

Estimation of 2:4-Dinitro-1-naphthol and Martius Yellow in Wool Fabrics. C. N. Tewari, S. C. D. Gupta, and B. C. Bera. *J. Sci. Ind. Research* (India), **7 B**, (9), 133–135 (1948): *Chem. Abs.*, **43**, 5956 (1949).

A spectrophotometric method of determining 2:4-dinitro-1-naphthol and its sodium or potassium salt, Martius Yellow, used for mothproofing wool, is based on percentage transmittance of a known wavelength through an aqueous solution of the dye. Different concentrations of purified Martius Yellow in distilled water were examined in a General Electric recording-type spectrophotometer through a glass cell giving 1 cm. thickness of liquid with a light transmission of 500 mμ. at room temperature. A standard reference curve was plotted, showing the percentage of light transmitted against known concentrations of Martius Yellow in g. per c.c. of aqueous solution, from which curve the concentration of a Martius Yellow solution can be obtained. The method fails in presence of impurities such as are usually present in wool felts. Satisfactory results are obtained by a modification of the A.O.A.C. method, which is described in detail. C. O. C.

Mechanochemical Methods for use with Animal Fibres. O. Ripa and J. B. Speakman. *J. Textile Inst.*, **40**, T 338–T 341 (May 1949).

One method of assessing damage to wool fibres is based on the measurement of the work of extension to 30%. This can be carried out in water at 22·2°C. without damaging their elastic properties. It has been suggested that damage in fact does occur. Experiments were carried out on fibres whose uniformity of cross-section was also measured. The results indicate that appreciable damage does not occur in either distilled water or 0·1N. hydrochloric acid. It is pointed out that if the diameter of the fibre varies the thinner sections will be subjected to an extension greater than 30%, and permanent damage will result. In such cases the extension must be suitably reduced. W. J. M.

Determination of the Cuprammonium Viscosity of Cellulose— II and III. M. I. Arkhipov. *J. Appl. Chem. (U.S.S.R.)*, **21**, 1107–1113 (Nov. 1948); **22**, 385–391 (April 1949).

Cuprammonium hydroxide preparations made from metallic copper by the action of air in presence of ammonia solution, and specified by various authorities as a solvent for cellulose viscosity determinations, are examined and found to be unsuitable for exact measurements, largely owing to their variable nitrous acid content. The preferred reagent is prepared from copper hydroxide and ammonia solution and is substantially free from nitrous acid. The copper hydroxide is made by the action of ammonia and caustic soda on a washed precipitate of basic copper sulphate. The proposed reagent has the following composition (g./litre)— copper 13·0, ammonia 200, sucrose 2. This has a higher ammonia content than the present standard solvent. It has a higher dispersing action and gives lower viscosity figures. It yields less variable results. The importance of a standard period of sufficiently energetic agitation is emphasised. A. E. S.

Analysis of Nylon and Related Polymers. M. Clasper and J. Haslam. *Analyst*, **74**, 224–237 (April 1949).

The method is based on the hydrolysis of the nylon followed by the determination of the proportion and properties of the resulting organic acid and base. Nylon 66 is hydrolysed by boiling 1 g. under reflux for 20 hr. with 20 ml. hydrochloric acid (1 vol. conc. acid sp. gr. 1·16 diluted to 5 vols. with water). The product of the hydrolysis is extracted for 6 hr. with ether in a continuous liquid–liquid extractor. The extract is evaporated, dried at 100°c., and weighed, and the acid identified by m.p. and equiv. wt. determination. The residual solution is evaporated, dried at 100°c., and weighed, the base hydrochloride being identified by m.p. and chlorine content. The application of the method to nylon 610, nylon 6 (caprolactam), formaldehyde-modified nylons, and copolymers is described. The hydrolysis of nylon 610 is difficult and only satisfactorily accomplished after reprecipitation in finely divided form from its solution in *m*-cresol. A method has been devised for the determination of adipic and sebacic acids and for the isolation of the pure compounds from the mixed acids derived from the hydrolysis of copolymers. W. K. R.

Quantitative Determination of Nylon in Mixtures. A. Agster. *Textil-Praxis*, **4**, 138–139 (March 1949).

The increasing use of nylon in admixture with other fibres has made it necessary to elaborate reliable methods for the analysis of such mixtures. Qualitative tests for the identification of Perlons L, T, and U are first reviewed. For quantitative estimations the most suitable solvent was found to be concentrated formic acid. A 1-g. sample of material is extracted with ether or benzene, dried to constant weight, treated with 50 ml. of cold conc. formic acid for 15 min. with occasional shaking, filtered, washed first with cold conc. formic acid, then with water for 3–5 min., and finally dried to constant weight. This method is suitable for mixtures of polyamide fibres (Perlon L and T) with wool, cotton, casein fibre, and viscose and cuprammonium rayon, the loss in weight of the second component being negligible. The method requires modifying when estimating polyurethane fibres (Perlon U). The hot formic acid which is required to dissolve this fibre causes an increase in the weight of admixed cellulosic fibres. This increase in weight is reduced by diluting the acid to 80% and by applying it at 70°c. for 10 min. Under these conditions wool suffers a loss in weight of 2%, cotton is unchanged, and viscose and cuprammonium rayons show an increase in weight of 4%. Mixtures of nylon with wool can also be analysed by dissolving the wool in boiling 5% sodium hydroxide solution, when the loss in weight of the synthetic fibre is negligible. Alternatively the synthetic fibre can be dissolved in cold 80% sulphuric acid, but the wool then shows some increase in weight. The formic acid method cannot be used for mixtures containing silk, which would itself be partly dissolved, but the method using 5% sodium hydroxide is suitable. The only method for mixtures containing acetate rayon is to dissolve the latter with acetone. F. A.

Rapid Identification of Fibres in Mixtures. H. Draxl. *Textil-Rund.*, **4**, 347–351 (Oct. 1949).

The material under examination is treated for 3 min. at the boil in a solution containing 1 g. Chloramine Orange G, 2 g. Chloramine Yellow, 1 g. Brilliant Blue FFR extra, 1 g. Eosine extra, 0·5 g. Celliton Pink R, and 1 g. Igepon T or other dispersing and levelling agent per litre. The individual fibres are stained in characteristic hues. B. K.

Identification of Melamine and Urea Resins. G. Widmer. *Textil-Rund.*, **4**, 279–288 (Aug. 1949).

Melamine and urea resins can be identified, whether present in soluble form or as finished products containing the resin in hardened form, by the preparation of characteristic crystalline derivatives which are detected by microscopical examination. Melamine resins are identified as melamine itself or its picrate, and urea resins as urea dixanthate. 17 photomicrographs and 5 references to the literature are given. B. K.

Investigation on Cellulose Reactions. VII—The Periodate Method for estimating the amount of easily Accessible Materials in Cellulose. T. Timell. (VI, p. 77.)